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Development of a Tunable Zeeman Spectrometer for Analysis of Toxic Organic Compounds

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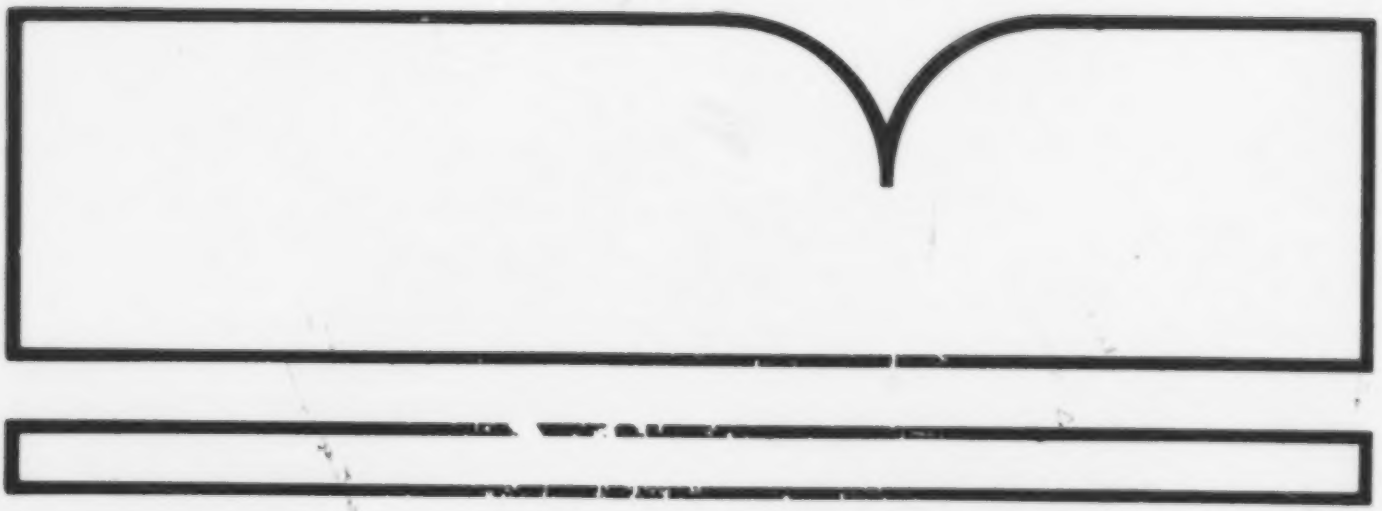

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DEVELOPMENT OF A TUNABLE ZEEMAN SPECTROMETER FOR ANALYSIS OF TOXIC ORGANIC COMPOUNDS

by

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This program was undertaken to investigate the application of a new high resolution ultraviolet-visible absorption technique called tunable atomic line molecular spectroscopy (TALMS) to the detection of a variety of volatile organic molecules of concern to the Environmental Protection Agency. During the first phase of the study a prototype instrument was built and tested to demonstrate the detection of both small (i.e., less than four atoms) and complex molecules. During the second phase a more compact instrument was constructed for delivery to EPA, Research Triangle Park, NC before January, 1982. This second instrument was optimized for the detection of the more complex organic molecules benzene and chlorobenzene.

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FOREWORD

Measurement and monitoring research efforts are designed to anticipate potential environmental problems, to support regulatory action by developing an in-depth understanding of the nature and processes that impact health and ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environment protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, has responsibility for: assessment of environmental monitoring technology and systems; implementation of agency-wide quality assurance programs for air pollution measurement systems; and supplying technical support to other groups in the Agency including the Office of Air, Noise, and Radiation, the Office of Toxic Substances, and the Office of Enforcement.

Analysis of organic compounds in the atmosphere is a difficult task requiring a variety of analytical techniques to ensure that identification and quantitation are valid. The environmental analyst requires methods that are precise, accurate and easy to implement. This study is concerned with the development of a new instrument which utilizes the information available in the high resolution absorption spectra of organic compounds in the ultraviolet and visible regions. The use of this instrument in analysis of organic compounds may greatly improve the analyst's capabilities to produce valid organic analysis.

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ABSTRACT

This research and development program was undertaken by the Lawrence Berkeley Laboratory to investigate the application of a new analytical technique called tunable atomic line molecular spectroscopy (TALMS) to the detection of a variety of volatile organic molecules of concern to the Environmental Protection Agency. The work can be described in two phases. In the first phase a prototype instrument was built and tested to demonstrate the detection of both small and complex molecules (a molecule composed of less than four atoms is referred to as simple and one composed of four or more is considered complex). In the second phase a more compact instrument was constructed for delivery to the EPA (Research Triangle Park) before January 1982. This second instrument was optimized for the detection of the more complex molecules.

TALMS is a high resolution, molecular optical absorption technique. It utilizes the splitting of an atomic emission spectral line from a lamp in a magnetic field (the Zeeman effect). One split line (Zeeman component) is made to overlap a rotational line of the analyte molecule by proper adjustment of the magnetic field. Other Zeeman components of this same atomic line that do not overlap the absorption feature are used as reference. The concentration of the molecule is then determined by differential intensity measurements of these two Zeeman components. TALMS was first developed to detect inorganic diatomic and triatomic molecules which exhibit well defined rotational spectra in the visible and ultraviolet spectral regions, e.g. NO, SO_2, NO_2. In general, the shorter the wavelength of absorption the higher the absorption coefficient, so TALMS should be a sensitive monitoring method in the ultraviolet and vacuum ultraviolet regions where all organic compounds absorb. Rationale for expected high specificity and high sensitivity with the TALMS instrument for large complex, organic molecules are discussed. Estimates of detection limits, resolution, selectivity, and linear range of the TALMS technique are also given.

Data on nitric oxide and formaldehyde are presented as a part of this study. The high resolution spectrum of formaldehyde is emphasized since this data led to the assignment of transitions in the formaldehyde molecule. During the second phase of this work, information was obtained concerning the line shape of the absorption features responsible for the benzene and chlorobenzene TALMS signals. Line shape information can be used to optimize the sensitivity of the instrument. Using this information, it was possible to build a second instrument with a magnetic field strength that was optimum for the detection of benzene. Benzene and chlorobenzene give a TALMS signal with the same atomic line. The line shape information allowed a field strength and field configuration to be chosen that would be relatively insensitive to chlorobenzene but still sensitive to benzene. The EPA instrument can be easily modified to obtain line shape information by installing an electromagnet.

This report was submitted in fulfillment of Interagency Agreement EPA-IAG-80-D-X1014 by the Lawrence Berkeley Laboratory under the sponsorship of the U.S. Environmental Protection Agency. This report covers the tasks of Phase I from May 1, 1980, to September 30, 1980 and Phase II from October 1, 1980, to September 30, 1981. Work was completed on September 30, 1981.

CONTENTS

Foreword.....iii
Abstract.....iv
Figures.....viii
Acknowledgements.....x

Section I: Introduction.....1

Section II: Conclusions and Recommendations.....5

PHASE I

Section III: Feasibility Study.....6

Rotational Fine Structure.....6
Expected Linewidth and Spacing For Typical Toxic Compounds....7
Formaldehyde.....7
Nitric Oxide.....11
Estimate of Lower Limit of Detection.....16
Estimate of Selectivity.....16

Section IV: Design of Instrument.....17

Lamp.....17
Electromagnet.....17
Monochromator.....20
Cell.....20
Detector.....20
Computer Interfacing.....22

Section V: Construction of Instrument.....24

General Layout.....24
Specifications.....24

Section VI: Optical and Mechanical Testing of the Instrument....27

Optical Linearity Test.....27
Electromagnet Calibration.....27

PHASE II

Section VII: Analytical Tests.....29

Gas Transfer.....29
Analytical Curve.....30
Search for TALMS Signals.....34
Line Shape Measurements.....35

References.....41

Appendices

Appendix I: Mechanical Diagrams.....42
Appendix II: Electronic Diagrams.....45

FIGURES

Number		Page
1	Tunable atomic line molecular spectroscopy a. molecular absorption line, b. Zeeman split line	4
2	Benzene: Band types I and II	8
3	Selected high resolution absorption spectra of large complex molecules	9
4	Low resolution, interferometric, and TALMS scan of formaldehyde 339.0 nm band	10
5	Zeeman scan of formaldehyde with Ag 338.3 nm line	12
6	NO absorption (γ) band and near coincident atomic lines	13
7	Relationship of Cd II 214.438 nm line to the electronic - vibrational - rotational lines of the (1,0) band, R_1 branch of nitric oxide	14
8	Relationship between the magnetic field strength and the differential absorption caused by NO for the Cd (II) line at 214.4 nm	15
9	Magnetically contained lamp	18
10	Low frequency discharge lamp	19
11	Block diagram of tunable atomic line detector optical assembly set to detect ultraviolet and vacuum ultra violet absorption	21
12	Current controlled retardation plate (phase squeezer)	23
13	TALMS experimental system	25
14	Block diagram illustrating mechanical and electronic connection of TALMS system	26
15	Magnetic field calibration of light source	28
16	Cell for TALMS calibration	31
17	Graphic display of benzene TALMS signal from HP-85	32
18	TALMS analytical curve for benzene	33

19 System for the measurement of sigma + and sigma - independently..... 37

20 Zeeman scan of benzene compared with high resolution spectrum..... 38

21 Zeeman scan of chlorobenzene..... 39

22 Block diagram of TALMS instrumentation..... 43

23 Photograph of the assembled TALMS instrument..... 44

24 Signal processing electronics..... 46

25 Front view of electronic module bin showing the manual controls..... 47

26 Circuit diagram of the TALMS lock-in amplifier designed and constructed at LBL..... 48

27 Circuit diagram for the lamp driver..... 49

28 Wiring diagram for the logarithmic amplifier. The instrument may operate with or without the automatic gain control feature shown in Fig. 26..... 50

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SECTION I
INTRODUCTION

Increased utilization of advanced technologies has led to the need to monitor a large variety of toxic organic and inorganic species. The identification and quantification of almost all organic compounds are presently accomplished using some type of chromatographic technique e.g., GC, GC/MS, HPLC, etc. These methods are time consuming, frequently not very selective, and, in the case of the GC-MS, require expensive equipment. A highly selective technique that depends on high resolution spectrometric principles would be faster and reduce the likelihood of incorrect qualitative analysis. The goal of this study is to develop an instrument to be used for highly selective and sensitive organic analysis. This instrument should ideally be compact, relatively inexpensive, and easy to operate.

The ideal analytical instrument would consist of a black box through which a sample is transported. The box would display the concentration of all species in any specified concentration range. Pretreatment of the sample would amount to simply transferring it from the outside environment into the instrument. Contrast this ideal with the present practice of performing tedious and elaborate separation procedures, which can only be carried out by an experienced chemist. For low level organic analysis this approach makes sample contamination or analyte loss a virtual certainty.

Those methods that depend only upon the interaction of radiation with the sample most closely approach the ideal case. Contamination and loss problems are greatly reduced when the sample is only moved into a light beam. The technique whose development is described in this report represents a step in this direction for the determination of both organic and inorganic species. Although non-gaseous samples must be volatilized to use this technique, this alteration is common in other types of organic analysis, e.g. GC, GC-MS, LC-MS.

An analytical technique called Tunable Atomic Line Molecular Spectroscopy (TALMS) has recently been developed at the Lawrence Berkeley Laboratory. It is capable of the detection and measurement of a large number of both organic and inorganic molecules with high sensitivity (Ref. 1). The selectivity of TALMS is such that molecules can be identified and quantified even in the presence of a large amount and numbers of interfering substances. Table I lists the molecules that have been investigated by this method and the atomic lines used. The number of compounds that can be detected is almost unlimited, depending only upon the presence of narrow, line like features in the absorption spectrum of the compound in the gas phase. This technique also requires minimal sample handling.

TALM spectroscopy consists of splitting a source atomic emission spectral line by means of a magnetic field (Zeeman effect) and making a differential absorption measurement between one Zeeman component that has been magnetically tuned to match an analyte absorption line and an unmatched Zeeman reference component. The difference in polarization between the Zeeman components permits the matching and nonmatching wavelengths to be alternately selected and the absorption measured very rapidly with an electro-

TABLE 1. Small Molecules Measured With TALMS

Molecule	Atomic Line	Wavelength (nm)	Transition
NO	Cd(II)	214.4	$^2S_{1/2}$-$^2P_{3/2}$
		226.5	
	Zn	213.8	$^1S_0$-$^1P_1$
OH	Bi	306.8	$^4S_{3/2}$-$^4P_{1/2}$
	Zn	307.2	$^3P_2$-$^3P_1$
I_2	Hg	546.1	$^3P_2$-$^3S_1$
S_2	Mg(II)	279.6	$^2S_{1/2}$-$^2P_{3/2}$
		280.3	$^2S_{1/2}$-$^2P_{1/2}$
SO_2	Zn	213.8	$^1S_0$-$^1P_1$
	Cd	228.8	$^1S_0$-$^1P_1$
NO_2	Cu	249.2	$^2S_{1/2}$-$^4P_{3/2}$
	B	249.7	$^2P_{1/2}$-$^2S_{1/2}$
		249.8	$^2P_{3/2}$-$^2S_{1/2}$
CH_2O	Ag	338.3	$^2S_{1/2}$-$^2P_{1/2}$

optical device called a Current Controlled Retardation plate (CCR). Referring to Figure 1, the line with label M=+1 is tuned with the magnetic field to exactly match the electronic-vibrational-rotational line of a specified molecule in the sample. The TALM spectrometer detects the difference in absorption between the M=+1 and the M=-1 reference Zeeman components. The differential absorption is then proportional to the amount of molecular species whose absorption line is matched by the M=+1 component of the source lamp. Thus, TALMS is a high resolution (high selectivity) absorption spectroscopy technique.

One remarkable feature of TALMS is its essential freedom from background interference. Since the difference in wavelength between the Zeeman components of the source emission line is typically 0.04 nm, any particle scattering or semi-continuous absorption will effect both components equally. Therefore, the differential absorption measurement will remove this interference from the total signal. Hence, this type of interference, which is a problem in most spectroscopic methods, does not affect TALMS measurements.

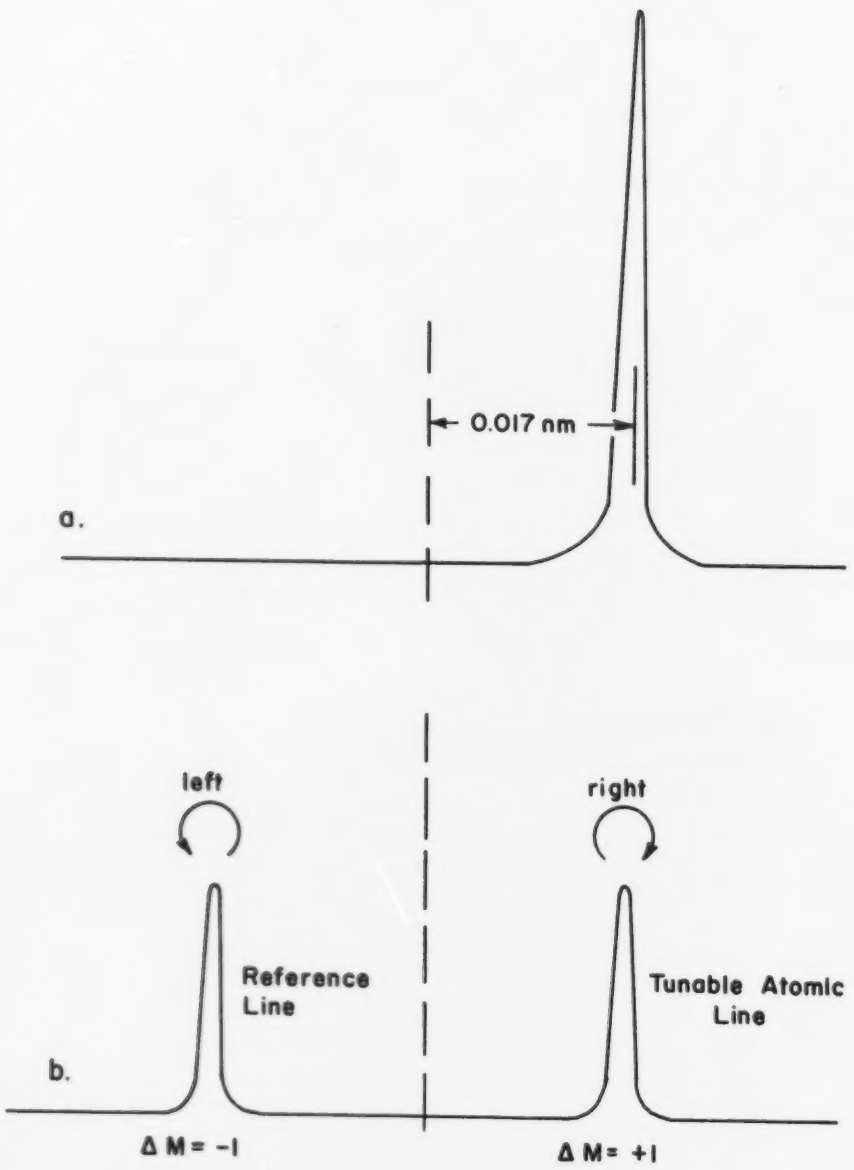

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Figure 1. Tunable Atomic Line Molecular Spectroscopy
a. Molecular Absorption Line
b. Zeeman split atomic emission line. Note: the $\Delta M = +1$ line is right-circularly polarized and the $\Delta M = -1$ line is left-circularly polarized.

SECTION II

CONCLUSIONS AND RECOMMENDATIONS

Tests with the TALMS system on diatomic, triatomic and tetratomic molecules indicate that these molecules contain rotational features similar in sharpness to that of atomic lines. Larger molecules, e.g. benzene at certain wavelengths, also show large changes in absorption intensity within a small 60 GHz (2 cm^{-1}) spectral interval. TALMS data, limited available data from ultra-high resolution absorption experiments and theoretical considerations make it evident that sharp line-like rotational structure and/or very sharp changes in the slope of absorption features are present in larger organic compounds and can be detected by TALMS. (Published spectra must be Doppler limited, e.g. resolution ca. 750,000, in order to adequately display regions that have sufficiently large changes in absorption to be detected by TALMS). To demonstrate this detection capability, a benzene and chlorobenzene detecting instrument has been constructed and will be delivered to EPA (Research Triangle Park) before January 1982.

The TALMS technique has a number of features that are useful for determining toxic organic substances. It utilizes a principle of operation that is totally different from the chromatographic methods now in use. Therefore it provides an independent confirming analysis. The sample pretreatment required for the TALMS method is much less than that required for chromatographic procedures. It should be possible to volatilize low boiling components from a solid or liquid sample directly into the light path of the instrument and perform the analysis with no further sample treatment. Because the application of TALMS analysis is simpler than chromatographic procedures, it should be possible to develop an instrument that requires less skill and experience on the part of the analyst. Samples may be sealed off in previously evacuated cells. These cells can be stored in the event another determination is required at a later date. These features make this method an important addition to the analytical techniques that are so essential to the task of monitoring our environment.

In order to utilize the TALMS technique effectively, a data base of atomic emission lines which match molecular absorption features must be constructed. The most logical way to do this is simply to make magnetic scans using emission lines from atoms that have the highest possible density of spectral lines in the region where molecular absorption is intense. The magnetic scan should be carried out automatically, and the molecular detection sensitivity should be tabulated for each atomic line. Such a search, if conducted manually, would be very tedious and time consuming. Thus, automatic search systems should be used. This can be accomplished using a simple computer interfaced with the electromagnet and the TALMS signal processor in such a way that data are automatically recorded with a minimum expenditure of the experimenter's time.

Future efforts should be directed toward fabricating high intensity light sources that produce as many emission lines as possible; toward production of the data base required for qualitative and quantitative analysis; and toward analysis of complex environmental air samples.

PHASE I

SECTION III

FEASIBILITY STUDY

ROTATIONAL FINE STRUCTURE

Molecular absorption in the vacuum ultraviolet (vuv), ultraviolet (uv), and visible regions is due to electronic transitions. The basic process involved in molecular transitions is the same as that in atomic transitions. Namely, a bound electron absorbs energy and is raised from a low molecular or atomic level to a higher level. However, since molecules are made up of a number of atoms, and therefore vibrational and rotational transitions occur, the absorption spectra of the simplest diatomic molecules are much more complex than the absorption spectra of the most complex atoms, such as uranium. Nonetheless, the molecular absorption spectra of simple molecules, diatomics and triatomics, are well defined showing a number of fine details in their vibrational-rotational spectra. Each rotational linewidth is comparable to an atomic absorption line width (approximately 6 GHz (0.2 cm^{-1}) at one atmosphere). This line width is about equal to the Doppler broadening. Molecules are distinguishable with high specificity by molecular absorption if the molecular absorption fine structure is resolvable. If the fine structure separation is less than the Doppler width, the molecular absorption is continuous and identification of molecules with high specificity is not possible from spectral measurements. For small molecules like NO, NO_2, SO_2, and H_2CO certain spectral regions are not Doppler limited and show discreet rotational lines.

Until 20 years ago, almost all spectroscopists, including the present principal investigators, would have said that there should be no discernable fine structure in the electronic-rotational-vibrational spectra of large molecules. The density of packing of the fine structure, which is due to transitions between rotational energy levels, is proportional to the moment of inertia of the molecule. Therefore, for large molecules, which have large moments of inertia, the packing of the fine structure should be quite dense. The number of rotational levels significantly populated at a given temperature also increases with decreasing spacing. Furthermore, nearly all large molecules are asymmetric tops and therefore should lack recognizable patterns of fine structure intensity.

However, beginning in 1959, there were several high resolution studies of the absorption spectra of complex molecules like benzene that showed line-like fine structure in several regions of the absorption band. It was these high resolution studies that led to the investigation and use of the TALMS technique for detection of complex molecules. How can such sharp absorption features exist in spite of the theoretical expectation of the impossibility of such an occurrence? The most reasonable theoretical explanation for this behavior is based on the concept of rotational line coincidences proposed by Hollas (Ref. 2). Hollas adopted the quasi-symmetric top approximation to a number of large asymmetric molecules and found several ways in which strong lines could coincide so as to produce readily

resolvable narrow features. Whether or not the Hollas interpolation is totally correct is not very important to the viability of TALMS. The most important feature is the experimental observation that complex molecules display line-like absorption spectra and these spectra are specific to certain molecules and no others.

EXPECTED LINE WIDTH AND SPACING FOR TYPICAL TOXIC COMPOUNDS

In general, there are two types of rotational-vibrational bands in large organic compounds that exhibit sharp structures (see Callomon et al., Ref. 3). These are shown in Figure 2 a-c. There are three distinctive features to note in a type I band: (1) a sharp edge on the high frequency side of the band; (2) an intense maximum of line-like sharpness about 1 to 2 cm^{-1} on the low frequency side; and (3) a shallow minimum about 3 to 5 cm^{-1} at still lower frequencies. Thereafter, at still lower frequencies a dense discrete structure extends with steadily diminishing intensity for about 60 cm^{-1}.

Type II bands have a single prominent feature - a maximum with a peak, again, of line-like sharpness (see Figure 2c). On the high frequency side of this maximum the intensity falls very rapidly to zero. On the low frequency side it first falls very rapidly and then degrades slowly and smoothly with copious fine structure.

All other bands in the spectrum appear to be variants of these basic types. These are illustrated in the spectra of benzene and other large molecules in Figure 3 (Ref. 4). The spacing between the fine structure lines is about 0.4 cm^{-1}; well resolvable in spite of Doppler broadening. Thus, the absorption spectra of these larger compounds contain features that distinguish them from one another. Hence, their detection can be achieved by means of high resolution instruments like TALMS having a resolving power better than the Doppler width.

FORMALDEHYDE

The formaldehyde molecule is a good choice for investigating the application of the TALMS technique to organic compounds. It is relatively small and exhibits well defined rotational structure. Figure 4 provides a comparison of the formaldehyde 3390 Å absorption band obtained using traditional low resolution spectroscopy (4a), high resolution interferometry (4b), (Ref. 5), and TALMS (4c). (All data were obtained with formaldehyde in the gas phase.) The superior resolution of TALMS shown in Figure 4c is responsible for the high degree of selectivity obtainable with this technique. Because this method monitors molecules by comparing intensities of Zeeman split atomic emission lines after passage through the sample, the higher the resolution the smaller the probability of interference by non-analyte molecules. The TALMS data in Figure 4c demonstrate an experimental resolution ($\lambda/\Delta\lambda$) of greater than 500,000. Yet, the data were obtained using equipment that would fit on the top of an office desk.

Verification of the authenticity of this data is provided by comparison with other experimental spectral studies and with theory. Rotational

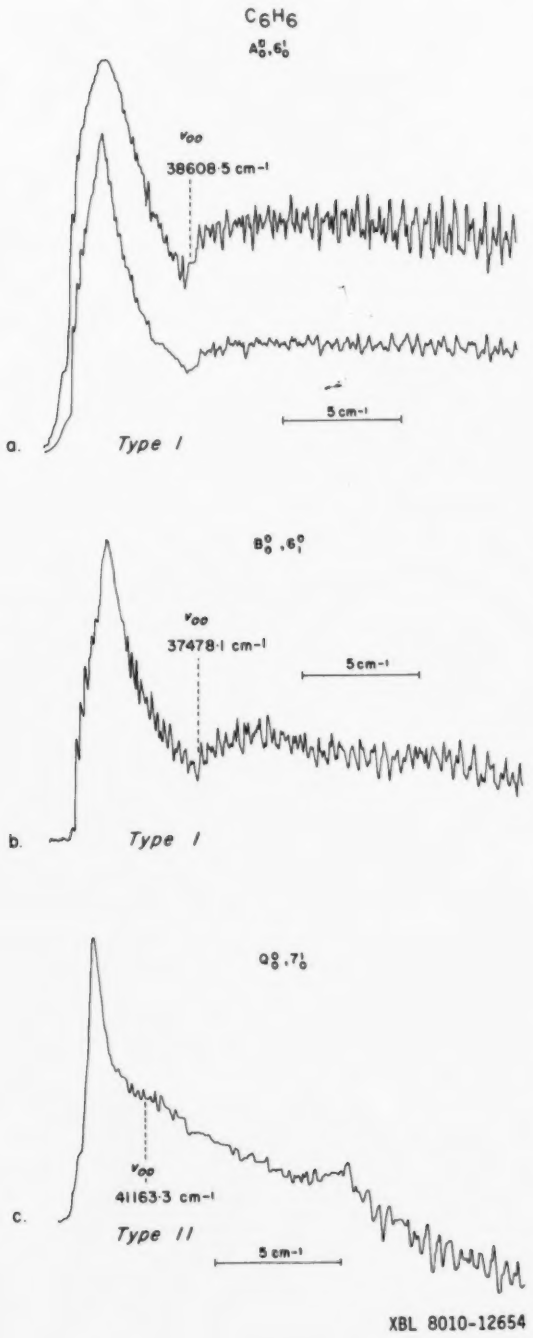


Figure 2. Benzene: Band types I and II.

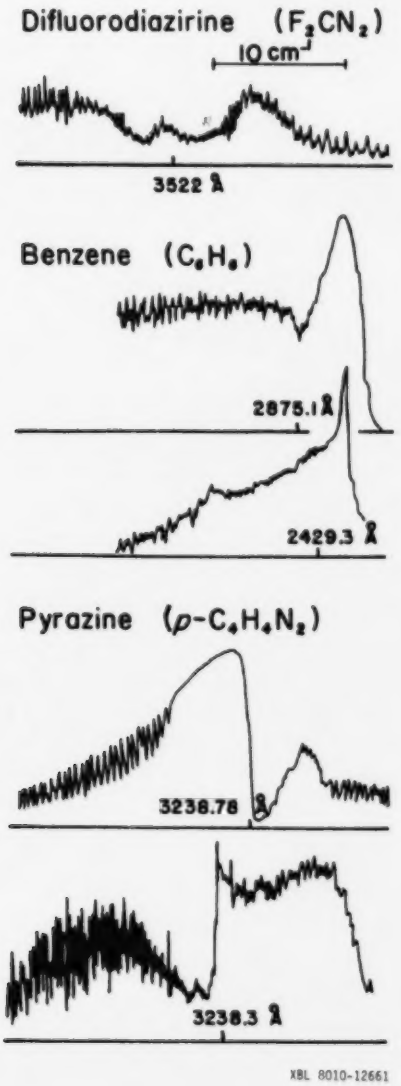
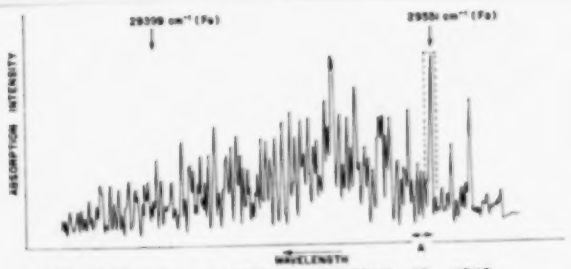
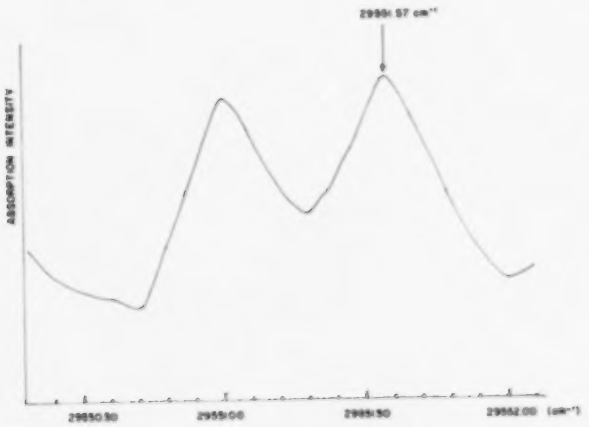


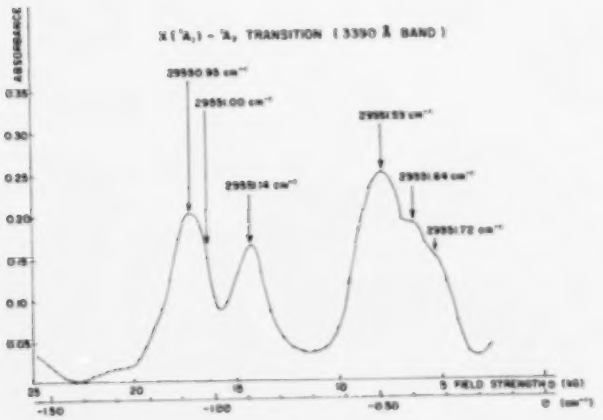
Figure 3. Selected high resolution absorption spectra of large complex molecules.



a LOW RESOLUTION ABSORPTION SPECTRUM OF HCHO



b FABRY-PEROT INTERFEROMETRIC SCANNING OF SECTION "X" ABOVE



c ZEEMAN SCANNING OF HCHO (Formaldehyde) BY Ag 3383 Å RESONANCE LINE

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Figure 4. Low resolution, interferometric and TALMS scans of formaldehyde 339.0 nm band.

structure in the formaldehyde molecule was investigated in a classic study by Dieke and Kistiakowsky in 1934 (Ref. 6). The TALMS spectrum from Figure 4c is enlarged and displayed in Figure 5 with the rotational quantum number assignments indicated. (A paper justifying these assignments has recently been accepted for publication by the Journal of Molecular Spectroscopy). This result was obtained by scanning the 3390 Å formaldehyde band with the 338.3 nm Ag line. At zero field the separation between the Ag line and the K"=3, J"=5,6,7 rotational lines of formaldehyde is only about 0.5 reciprocal centimeters. It is interesting to note that the three lines, K"=3, J"=5,6,7, could not be resolved by Dieke et al., even with a 40 foot spectrograph. This figure illustrates the availability of absorption peaks for the TALMS technique for small organic compounds even in a small (1.5 cm^{-1}) spectral range.

NITRIC OXIDE

Figure 6 shows a vibrational band of NO (γ-band) and the Zn and Cd atomic emission lines in the same spectral region. It is clear that Zn I at 206.1 nm, Cd II at 214.4 nm and Cd II at 226.5 nm all lie close to the vibrational-rotational absorption lines of NO and may be brought into an exact coincidence by Zeeman tuning. The Cd II line at 214.4 nm should give the highest sensitivity at room temperature.

Figure 7 represents the detailed structure of the (1,0) vibration band showing the individual rotational lines. The wavelength of an atomic emission line must be adjusted to accurately match one of these rotation lines. As shown in Figure 7, the Cd II line at 214.43 nm comes within 0.019 Å of the R (27/2) line. The left circularly polarized Zeeman component can be brought into exact coincidence with this transition using a magnetic field of 9.2 kG. Similarly, the Cd II line at 226.4 nm and Zn I 213.8 nm line can be brought into exact coincidence with other electronic-rotational-vibrational transitions of NO. Figure 8 illustrates the experimental results obtained by plotting the differential absorption as the magnetic field strength was varied from 0 to 20 kG for incident Cd II light normally at 214.43 nm. A minor peak in the curve was observed at a field strength of 5.3 kG because of the presence of another Zeeman component with the same circular polarization having a slightly different frequency. We see that the optimum field strength for monitoring this molecule is 9 kG.

Loss of light by scattering or molecular absorption does not significantly influence the differential absorption signal tuned to the NO rotational line. While monitoring the signal produced by the 214.43 nm Cd II line, the light passing through the system was first partially absorbed by nitrobenzene and then by acetic acid vapor. No change in signal occurred even when as much as 60 % of the light was absorbed. A similar result was obtained when 60 % of the light was scattered by inserting a cell containing smoke in the optical path. This is a unique feature of Zeeman tuning that distinguishes it from other techniques and makes its use extremely promising for monitoring specific molecules in complex mixtures.

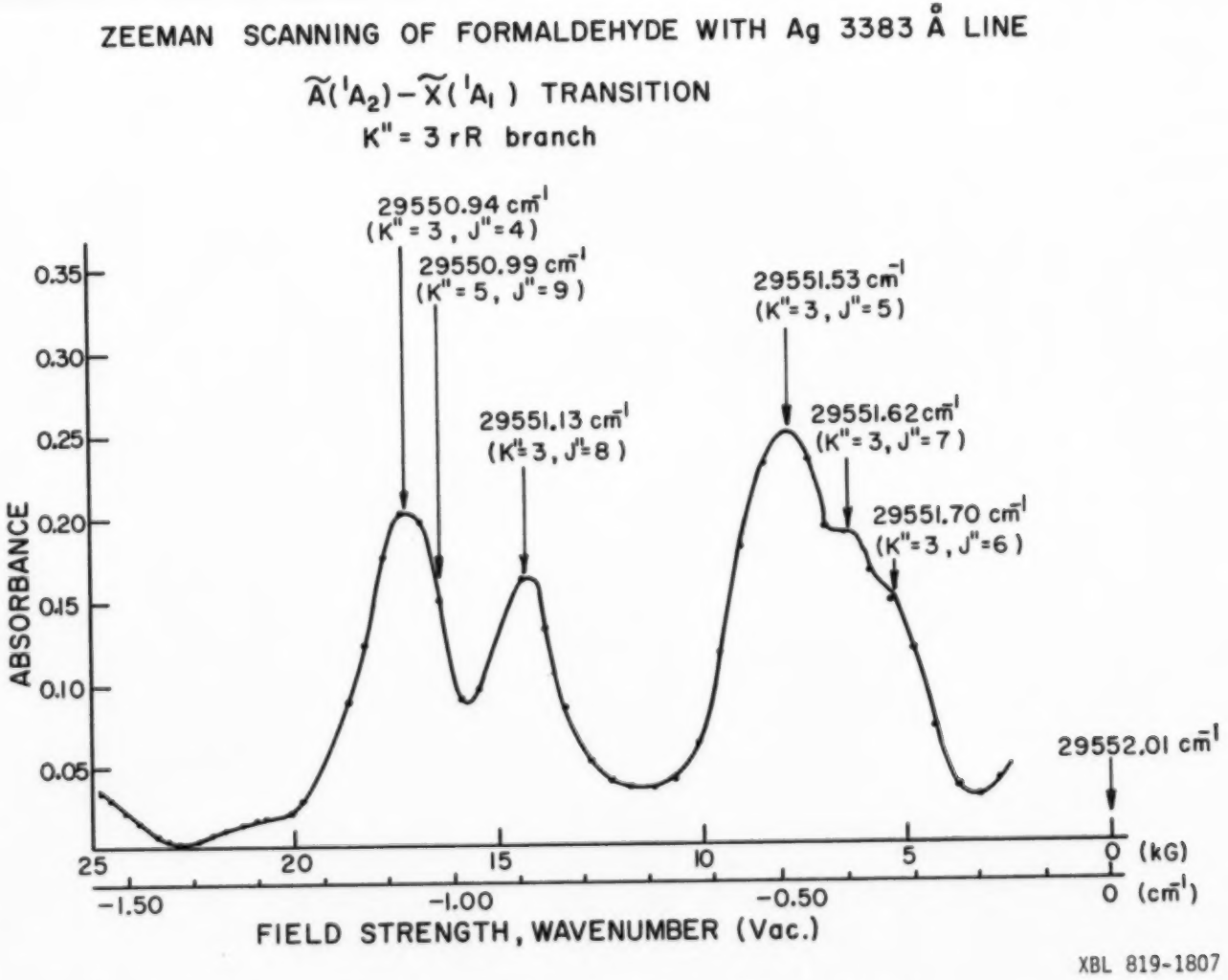

Figure 5. Zeeman scan of formaldehyde with Ag 338.3 nm line.

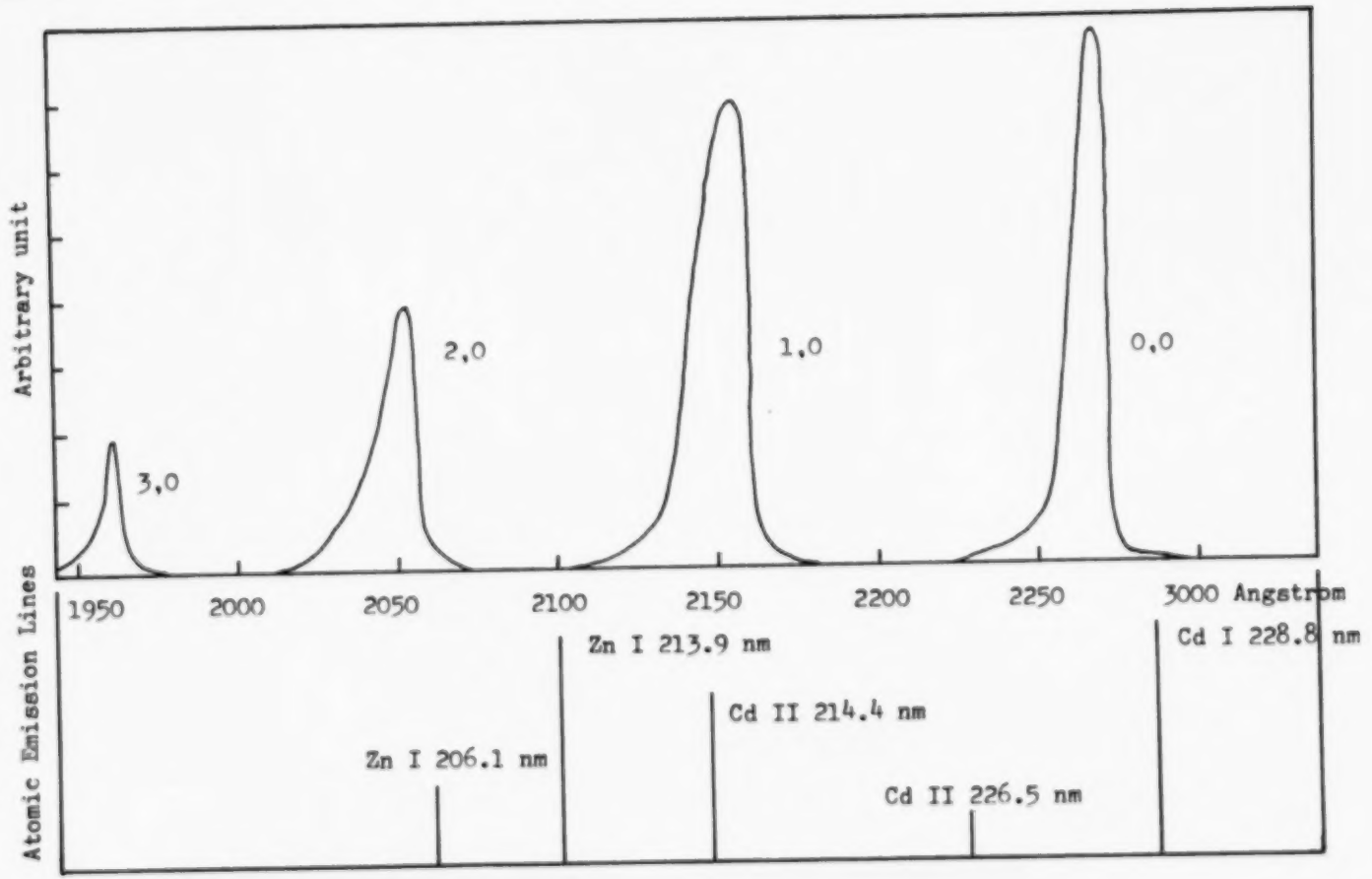

Figure 6. NO absorption (γ) band and near coincident atomic lines.

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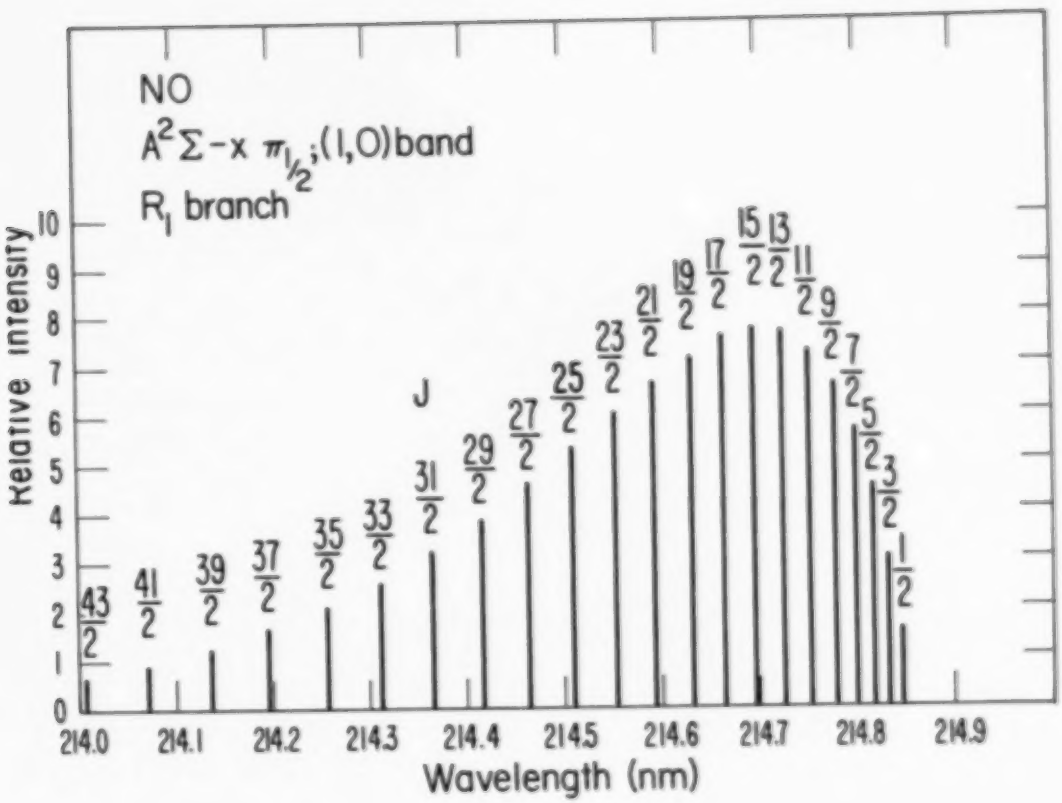

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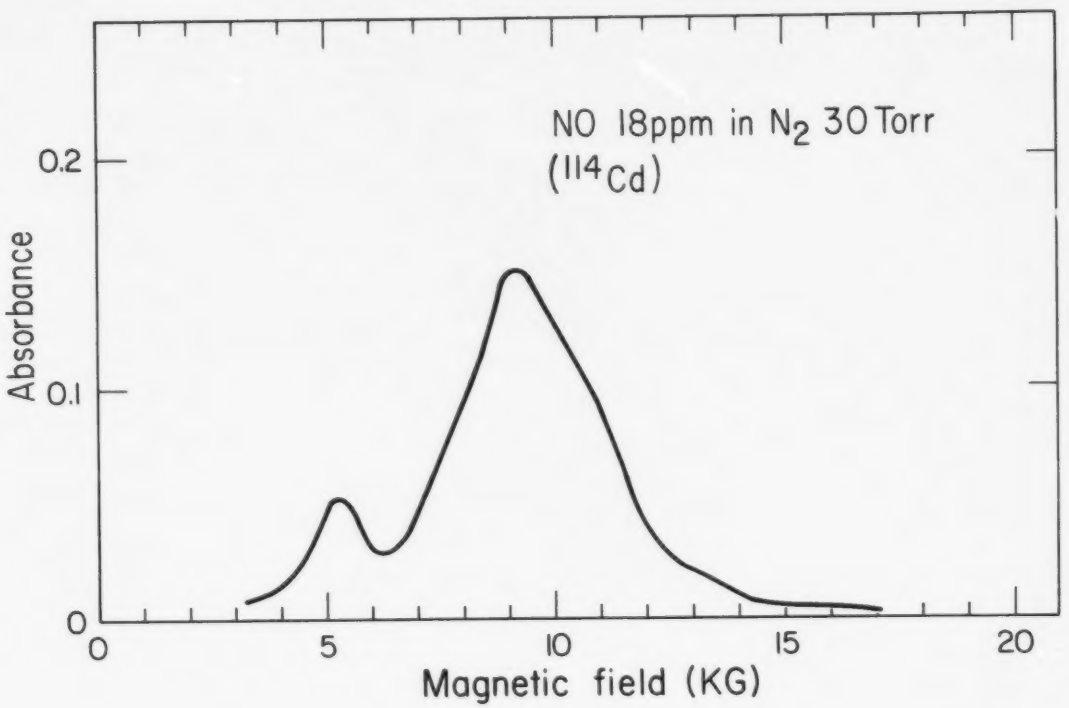
Figure 7. Relationship of Cd II 214.438 nm line to the electronic-vibrational-rotational lines of the (1,0) band, R_1 branch of nitric oxide.



XBL 795-1605A

Figure 8. Relationship between the magnet field strength and the differential absorption caused by NO for the Cd(II) line at 214.4 nm.

ESTIMATE OF LOWER LIMIT OF DETECTION

The TALMS lower limit of detection for diatomic molecules is about 50 ppb per meter pathlength and for the triatomic molecules investigated is about 1 ppm per meter. The present TALMS instrument uses a 0.3 meter McPherson monochromator which has an effective 1.2 meter optical path length. Hence, the above sensitivities of 50 ppb and 1 ppm can be easily achieved if there is sufficient sample. The lower limit of detection for polyatomic molecules is difficult to estimate. Because the existence of sharp pseudo line-like structure in polyatomic molecules is now interpreted as the overlapping of many individual rotational lines, the expected lower limit of detection should be similar to that found in diatomics. However, only further experimentation can provide a definite answer to this question.

ESTIMATE OF SELECTIVITY

Selectivity depends on the resolving power of the instrument and the band width and spacing of the rotational lines or pseudo-line structures in the absorption spectrum of the compound sought. TALMS resolving power is determined by the atomic emission line width. The light source used with the present instrument produces line widths of 2 GHz which corresponds to 0.07 cm^{-1}. Most molecular absorption takes place at about 2500 Å which corresponds to 40,000 cm^{-1}. Thus, the inherent resolving power of the instrument is 40,000/0.07 = 600,000. This resolving power is higher than the resolution required to measure Doppler broadening. Therefore, the resolution available from TALMS is sufficient to detect any molecular absorption structure, if it exists. To determine one molecule in the presence of another there must not be accidental coincidence of sharp features within 0.07 cm^{-1}. The probability of this happening when detecting atoms is almost zero because atomic absorption lines do not fall within 0.07 cm^{-1} of each other. For smaller molecules with relatively large spacing between rotational lines, almost complete confidence can be placed in accurate speciation information based on one rotational line. For larger complex molecules, e.g. benzene, selectivity is also almost certain since the existence of sharp absorption lines is believed to be due to the overlapping of many rotational transitions of the same molecule. Such overlapping can only take place at well-defined wavelengths determined by the molecular parameters of a molecule and therefore is very specific to that molecule. Thus accidental coincidence by other complex molecules within the wavelength interval used by TALMS is extremely unlikely. In the rare event of overlap of fine structure by other molecules at one wavelength, another atomic emission line can be used. Such a process can be used to increase the selectivity until there is no question about the identity of the species.

SECTION IV
DESIGN OF INSTRUMENT

The design of this instrument is best described by considering the individual components. These are the lamp, electromagnet, monochromator, absorption cell and detector.

LAMP

The proper performance of the TALMS system depends on the quality of the light source used. Although there is practically one atomic emission line for every angstrom of the ultraviolet and visible spectral region (Ref. 7), the line intensities are generally not very high. In order to obtain a good signal to noise (S/N) ratio, it is necessary to have high line intensities. Extremely intense atomic lines have been produced by a specially designed light source (invented by T. Hadeishi and patented under his name) called a magnetically contained arc discharge lamp. This light source has been highly refined over its original form and is now simple to operate. The magnetically contained lamp (MCL) produces emission lines at least two orders of magnitude brighter than commercial hollow cathode lamps. Because of the interchangeable nature of the cathode, it is extremely inexpensive to operate. However, the most important feature of this lamp is the capability for operation at very high power and at reduced gas pressures. This leads to very high intensity from otherwise weak atomic emission lines. Figure 9 shows a photograph of the earlier version of the MCL light source. A Cajon connector is used to connect the lamp to the vacuum system and this connection need be only finger tight to obtain a vacuum tight connection. Assembly and disassembly as many times as desired is thus assured without detrimental effect to the vacuum connection. The typical operating life of the cathode at extremely high power is about 40 hours. The cathode can be replaced in less than 5 minutes.

In addition to the MCL, a sealed off lamp system which operates continuously for about one year has been developed for various elements. In fact, the benzene data described later were obtained using such a lamp emitting Cu and Hg lines. The main difference between the MCL and the sealed low frequency discharge lamp (LFDL) is the latter operates similarly to an electrodeless discharge lamp (EDL). The LFDL emits very intense resonance lines but a much smaller number of lines than other types of discharges. The advantages of the LFDL over the MCL are its extremely long life and high intensity resonance lines. Hence such lamps should be used to determine those toxic molecules occurring at low concentrations whose sharp molecular absorption lines match resonance lines. Figure 10 illustrates the construction of the LFDL.

ELECTROMAGNET

A specially modified magnet made by Eastern Scientific Instrument Company (Model 7) was used to shift the wavelength of the MCL and the LFDL. This precision laboratory electromagnet contains four inch pole pieces and an adjustable air gap. A major modification of the magnet was made by

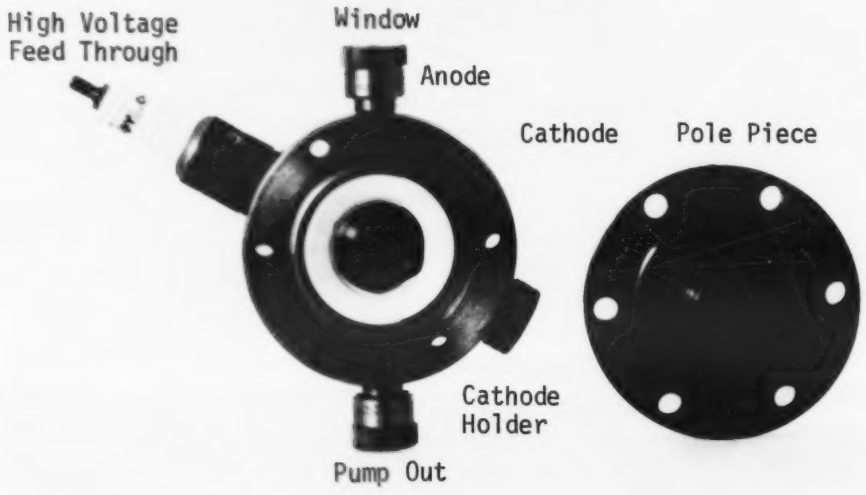


Figure 9. Magnetically contained lamp.

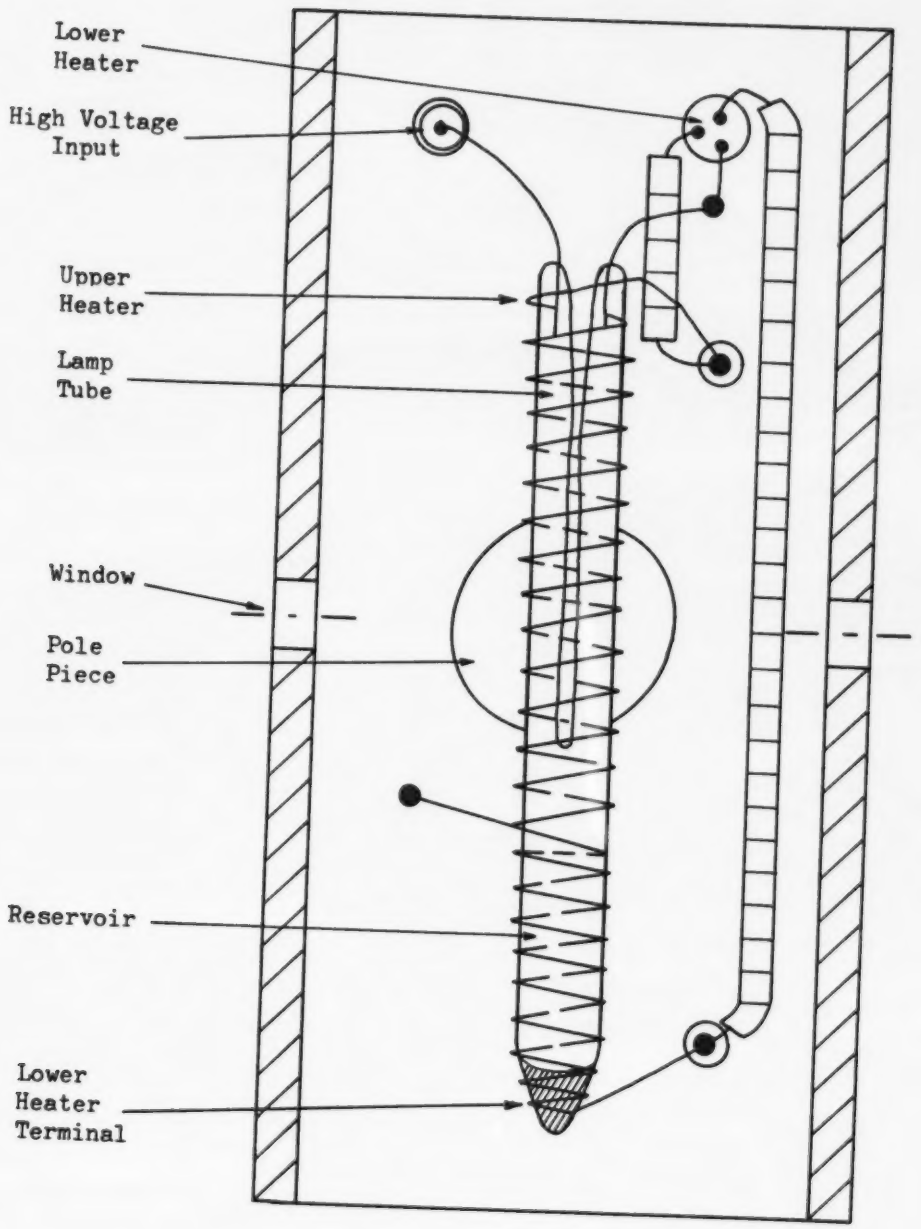


Figure 10. Low frequency discharge lamp.

opening a hole through a pole piece so that atomic lines emitted in a direction parallel to the magnetic field could be used. Also the MCL and LFDL were placed in a container with a lens for collimating light from the emission point. In this way a maximum amount of light could be passed through the small diameter but long path hole in the pole piece. The high precision alignment required for this operation was achieved by using a laser beam. The magnet system was also modified by interfacing the power supply with a computer. This modification improved the S/N ratio and produces data that indicate whether TALMS is detecting a sharp line or a sharp change in the slope of an absorption feature. Computer control was also used for automatic data gathering. A rather interesting approach to computer control involved coupling an inexpensive personal computer (HP-85) to a commercially available general purpose interface bus (GPIB) device. With such a device, no hardware construction for electronic control is necessary. The details of this interface are described below. With computer control, little experience is required to operate this rather sophisticated device.

MONOCHROMATOR

A McPherson Model 218, 0.4 meter, scanning monochromator is used in this system. The main reason for this choice is the crisscrossed optical design, which creates an effective absorption path length inside the monochromator of 1.2 meters. This instrument also possess a large acceptance angle (small f-value) because of its short (0.4 meter) focal length. The range covered is 1050 Å to 10,000 Å (vacuum ultraviolet to visible), and the spectrum is dispersed with a 1200 G/mm grating. Because of the monochromator's rugged construction all the critical optical components can be rigidly attached with little possibility that vibrations or shock will cause misalignment. The scannable wavelength range covers most of the vacuum ultraviolet transitions that occur in toxic organic compounds as well as the usual visible and ultraviolet spectra.

CELL

Several versions of absorption cells were constructed and tested. These ranged from very simple quartz cells to a more complex cell with a quartz window fitted to a Varian Con-Flat system. The cells were connected to a vacuum system so that the vapor density and buffer gas pressure could be varied as desired. An ultra-high precision MKS Baraton Type 170 differential membrane capacitance manometer was used to monitor the absolute pressure of the gas vapor in the cell. Because the pressure sensor can be baked out, absolute vapor pressure of various toxic compounds can be measured without condensation on colder regions of the cell.

DETECTOR

Figure 11 shows the experimental set up. A Hamamatsu extended range photomultiplier tube could be used over the entire spectral range with a fluorescent coating on the face of the tube so that it would respond in the vacuum ultraviolet (vuv) region. LiF optical components can be used

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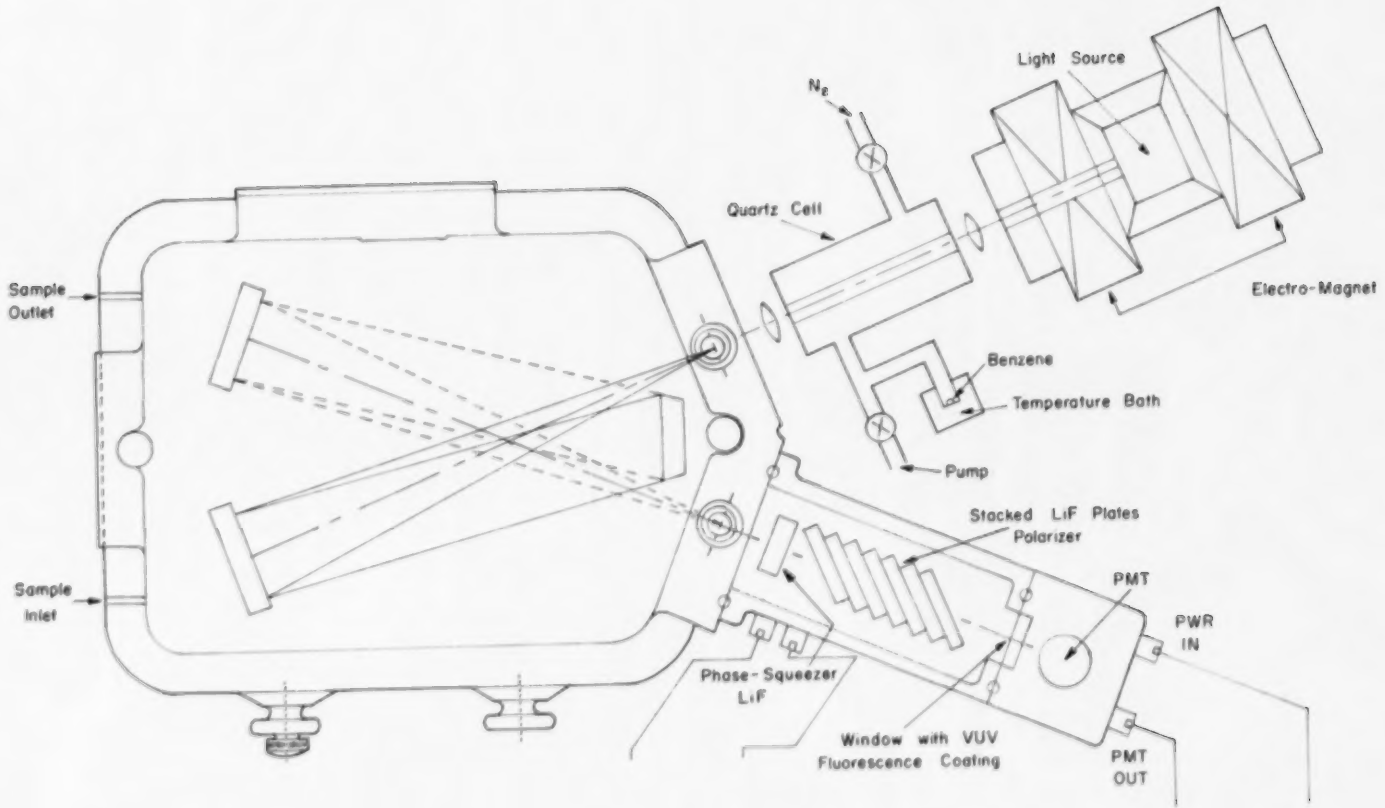

Figure 11. Block diagram of Tunable Atomic Line Molecular Detector optical assembly set to detect ultraviolet and vacuum ultraviolet absorption.

throughout, including the current controlled retardation plate, because this is one of the few materials with high transmission in the vuv region. In experiments thus far, where only the region above 1800 Å was of interest, high purity quartz (Suprasil) optical components were used. See Figure 12 for details of the current controlled retardation plate.

COMPUTER INTERFACE

As already indicated, the instrument was interfaced to a computer both to simplify the storage and manipulation of data as well as to automatically scan the magnetic field. A HP 6942A bin was used to connect the HP-85 computer to the TALMS through a IEEE bus. This bin can accept as many as 16 cards but only two are used for data manipulation and storage. One card is an analog to digital converter. The other card can both multiplex analog signals and generate digital signals. The functions of this card are initiated upon instruction from the HP-85 and can both be performed simultaneously. This multiplexer, signal generator, card contains 16 relays (Model 69730A) with each relay port available. Although this system would be too bulky for a field instrument, it is ideal for a research instrument that is used on a variety of problems (e.g. the determination of line shape as well as optimum parameters for routine monitoring).

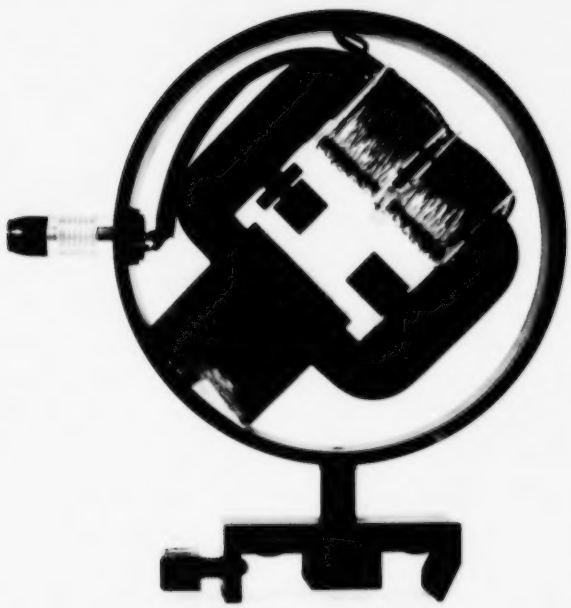

Figure 12. Current controlled retardation plate (phase-squeezer).

SECTION V

CONSTRUCTION OF INSTRUMENT

GENERAL LAYOUT

Figure 13 shows the components of the experimental TALMS system as originally used in the laboratory. The instrument eventually produced was much more compact. The entire electronic system for signal processing was designed and fabricated to meet the special requirements of the TALMS system. Figure 14 is a block diagram of the electronic connections to the TALMS spectrometer. Appendices I and II contain further photographs and diagrams of this system.

SPECIFICATIONS

The TALMS system was designed for wavelength tunability by utilizing the Zeeman effect with a magnetic field strength of 0 to 25 kG. For atomic emission lines with g values of 1.5 like the Hg 2537 Å resonance line, a 25 kG magnetic field will give a wavelength separation between the long and short wavelength Zeeman components of 100 GHz (3.3 cm^{-1}). Thus, any sharp change in the absorption spectrum of a compound that occurs within a 3 cm^{-1} interval of the atomic transition line can be used to detect that compound. The prototype instrument is designed so that it can easily fit on the top of a desk.

Figure 13. TALIS experimental system.

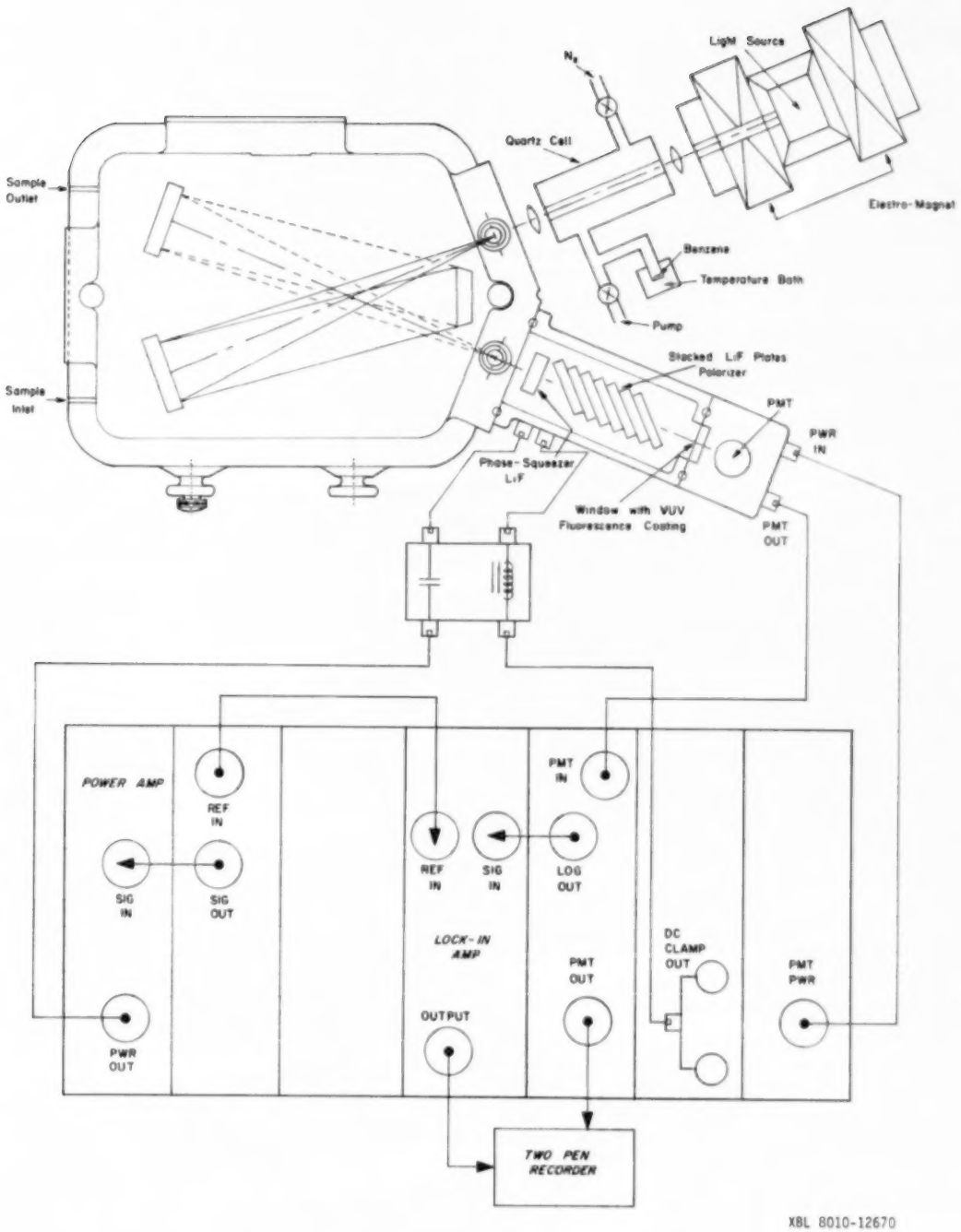

Figure 14. Block diagram illustrating mechanical and electronic connection of TALMS system.

SECTION VI

OPTICAL AND MECHANICAL TESTING OF THE INSTRUMENT

OPTICAL LINEARITY TEST

A logarithmic relationship (Beer's law) exists between molecular concentration and the alternating differential absorption signal. However, as the amount of light absorbed becomes greater, this relationship breaks down. (This is the same effect as that observed in atomic absorption spectroscopy). Because of this, the calibration curves will be linear only if no more than ca. 75 % of the light is absorbed. A simple logarithm curve fitting routine, such as that provided by a small programable calculator, can extend the linear range to 95 % absorption. In a practical case, the level of absorption by the sample can be adjusted by means of gaseous dilution so that a perfectly linear range can be selected using standard logarithmic detection methods. However, it is doubtful that the system will be required to operate in the non-linear region for the low concentrations encountered in ambient air.

ELECTROMAGNET CALIBRATION

Figure 15 shows the relationship between electromagnet current and field strength taken with the magnetic field sensor inside the light source. Measurements were taken by sensing the magnet current across a shunt with a HP-3438 Digital Multimeter that was interfaced to a HP-85 computer along with a Rawson gauss meter so that simultaneous readings were printed out digitally. Once this curve was constructed, readings of magnet current could easily be converted to magnetic field strength.

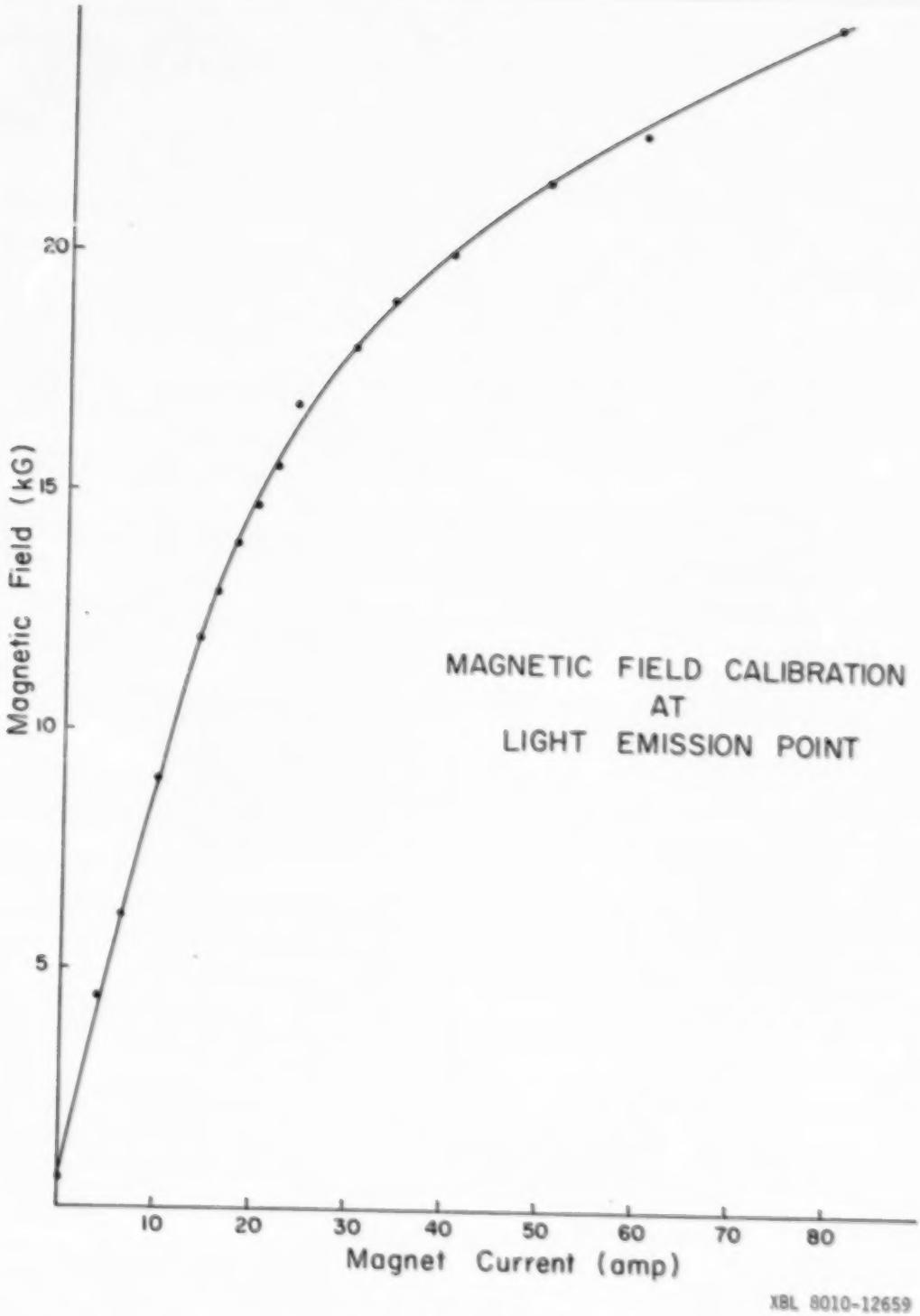

Figure 15. Magnetic field calibration of light source.

PHASE II

SECTION VII

ANALYTICAL TESTS

GAS TRANSFER

The analytical curve for TALMS results from measurements of the signal strength with differing known amounts of organic vapor in the light path. In order to obtain known amounts of vapor in the instrument, it was necessary to be aware of some details of gas transfer. A cell was built that contained a storage tube for the compound of interest. By immersing this tube in a constant temperature bath, it was possible to control the vapor pressure and hence place a known concentration of molecules in the light path. Figure 16 is a schematic of the cell designed for this purpose.

This cell contains a port for mounting the tube containing the compound of interest, a vacuum port, and a valve between the cell and the vacuum pump. The compound containing tube is immersed in liquid nitrogen (LN) and the system is evacuated. While the system is still open to vacuum, the LN bath is exchanged for a bath that will produce the desired vapor pressure of compound. When an indication of signal is noticed, the valve to the vacuum pump is closed and the cell rapidly approaches equilibrium. If equilibrium is not obtained, there will be a slow, exponential drift both of the TALMS signal and the percent transmission level to the equilibrium value.

Cell evacuation is necessary because diffusion processes are so slow. The rate of diffusion of component a, in the direction z, across a plane of unit cross section is given by the expression:

$$N_a = - D_{ab} (dC_a)/(dz)$$

Where N_a is the diffusion flux across a unit area normal to the z direction in moles/(cm^2 sec), D_{ab} is the diffusion coefficient of a in b in cm^2/sec, C_a is the concentration of a in moles/cm^3, and z is the distance in the direction of diffusion in cm. As diffusion continues, the difference in concentration, dC_a, between points separated by the distance z, decreases. This causes the diffusion flux, N_a, to also decrease. The change in concentration with time approaches zero in an exponential fashion which means that N_a will also have an exponential time dependence. The small value of the diffusion coefficient (D_{ab} will be of the order 0.1 to 1 cm^2/sec) along with this exponential dependence means that long times are required to attain equilibrium. This would result in long times being required to obtain the data needed to construct an analytical curve.

Although diffusion times are long, the time required for molecules to move into an evacuated region are short. As the tube containing benzene warms up, the vapor pressure increases. Since the evacuation port is open, the molecules rapidly move through the cell. Under these conditions, the density everywhere in the cell closely follows the density just above the benzene supply. If there is no pressure difference between the benzene

supply and the vacuum port, equilibrium will be instantaneous when the vacuum valve is turned off. However, pressure differences will exist if there are long lengths of small diameter tubing in the system. The cell in Fig. 16 was designed to minimize such pressure differences and the data for the analytical curve were obtained without having to wait for the system to slowly approach equilibrium. When the higher vapor pressure points were obtained it was found that the vacuum valve should not be in the wide open position. At these higher temperatures the benzene in the bath was a liquid rather than a solid. If the liquid were exposed to a good vacuum, droplets of material were swept into the cell. The system would then approach equilibrium from a high vapor presure to a lower one as the benzene diffused to the tube in the bath. This is a very slow process. This situation was avoided by throttling the vacuum valve.

ANALYTICAL CURVE

The following procedure was followed to obtain data for the analytical curve.

1. The compound to be investigated is placed in a Pyrex tube which is connected to the cell assembly with a vacuum tight Cajon connector.
2. The side arm is next immersed in a LN bath and the system is evacuated.
3. This side arm is then immersed in a bath whose temperature has a known value and is constant; the vacuum valve is turned off when a signal begins to appear.
4. A signal level is obtained by recording the photomulitplier voltage over a several minute time interval.
5. The side arm is next immersed in a LN bath and the system is again opened to the vacuum pump.
6. Again a signal level is obtained over a several minute time interval.
7. The difference between the average signal at the known temperature and the average signal of the evacuated cell is determined.
8. The vapor pressure of the compound is calculated from empirical equations that relate vapor pressure to temperature.
9. An analytical curve is obtained by plotting the TALMS signal vs the vapor pressure.

The HP-85 computer was programmed to greatly simplify the data manipulation required by these operations. This system records on cassette tape the voltages corresponding to the TALMS signal and the blank signal. The voltage records are made at a time interval selected by the operator. After the run is complete, the HP-85 processes the data to produce a graphic display and averages the signals which allows the difference signal to be readily obtained. A typical display is reproduced in Fig. 17. In this case the cell was evacuated after 640 seconds (8 units on the x axis). The average value of the TALMS signal with benzene in the cell was 5.67×10^{-2} volts and the average value after evacuation was 8.56×10^{-4} volts. These values were automatically calculated and printed on the graphic display.

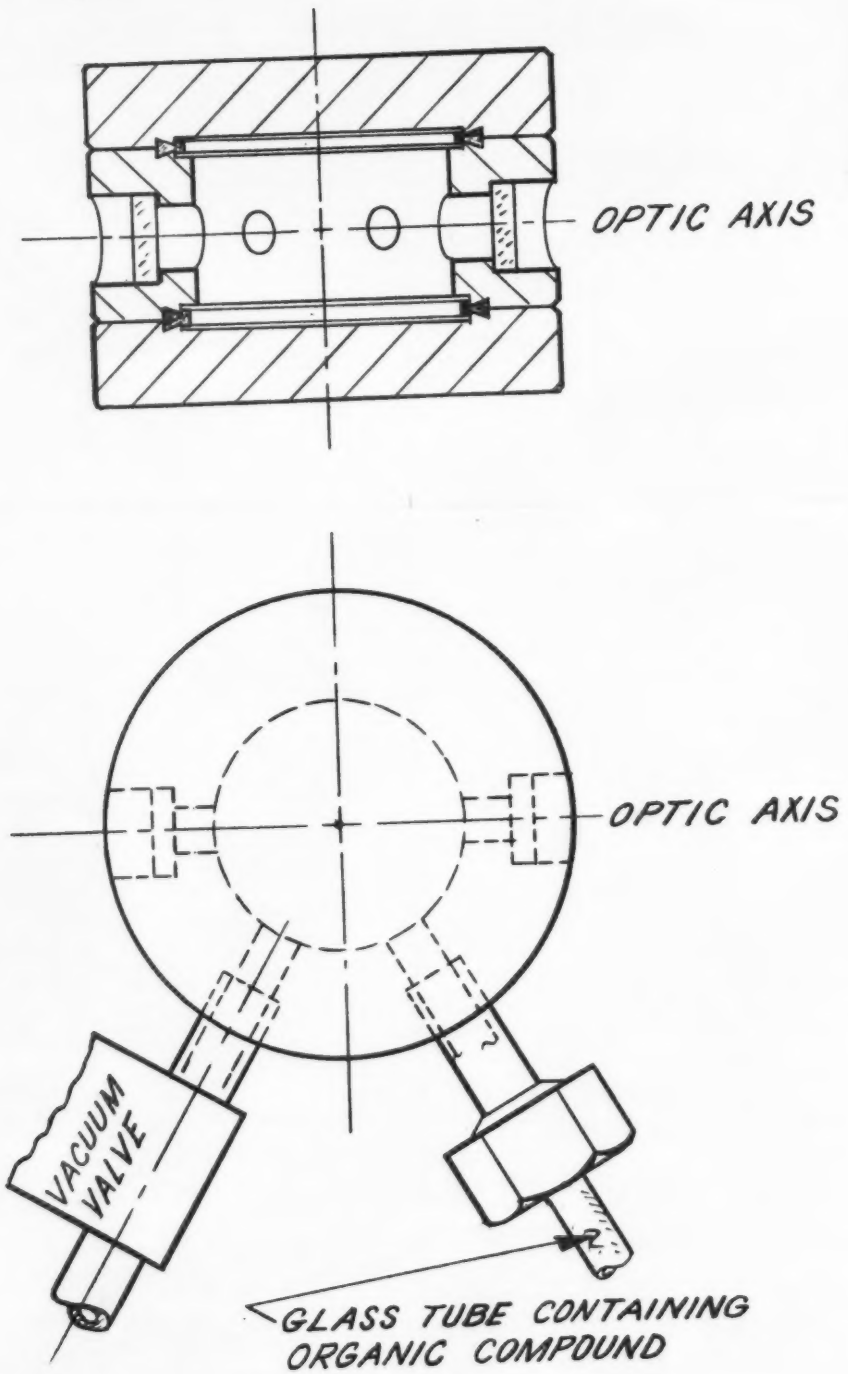

Figure 16. Cell for TALMS calibration.

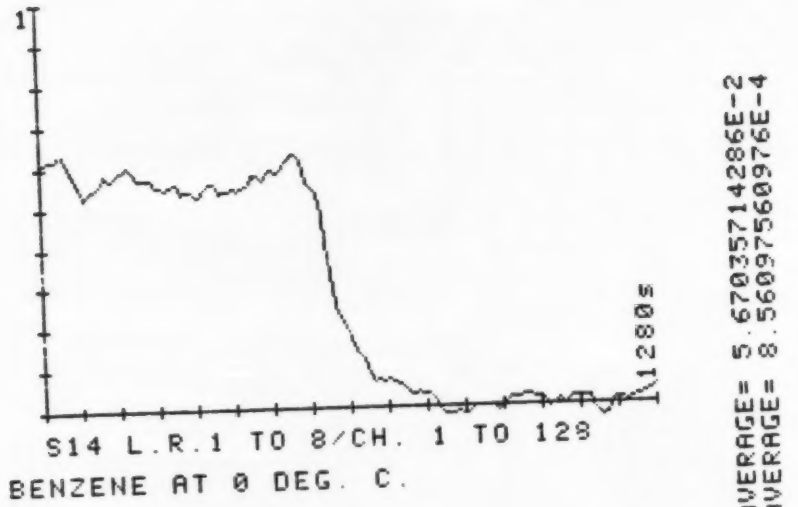

Figure 17. Graphic display of benzene TALMS signal from the HP-85.

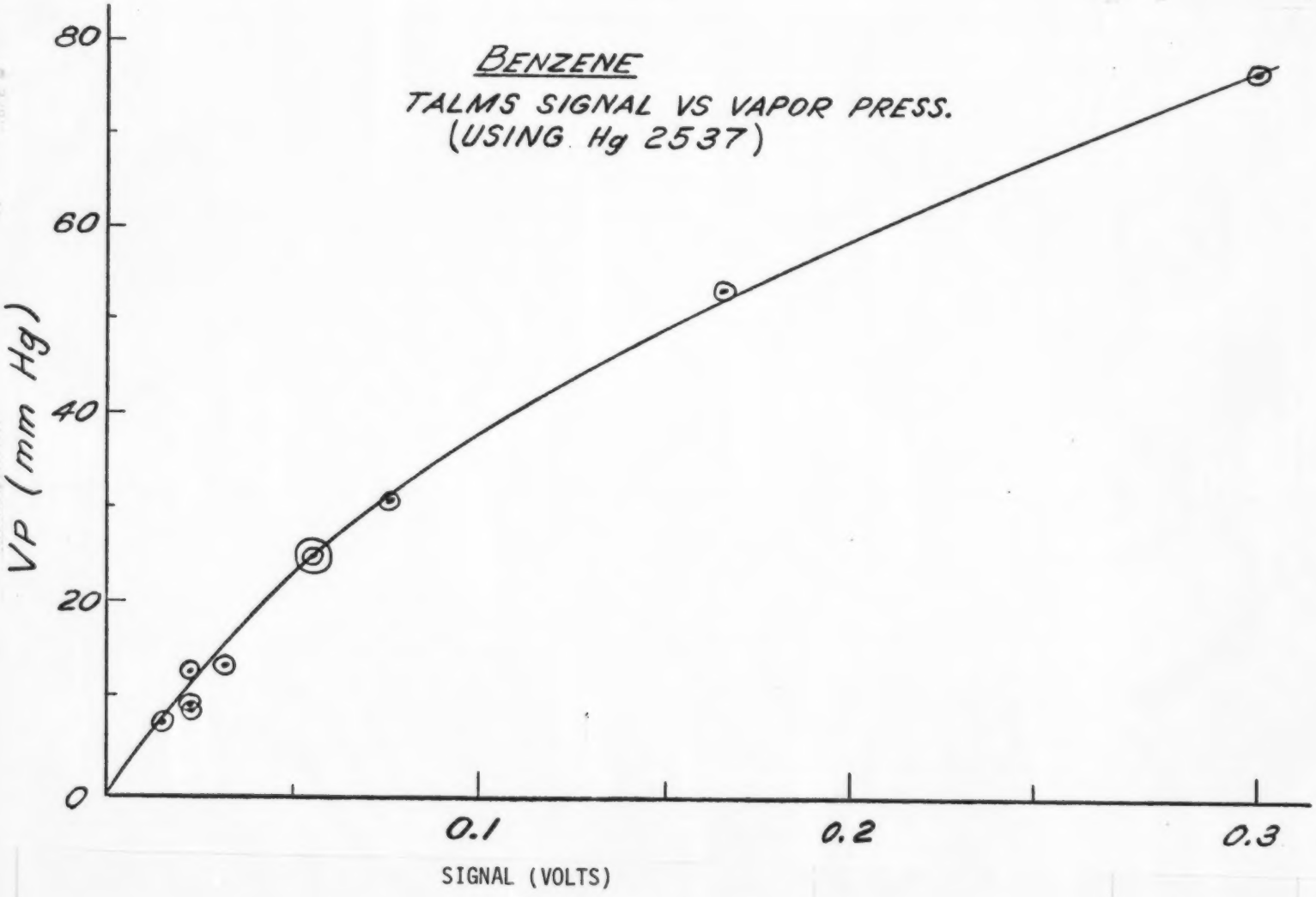

Figure 18. TALMS analytical curve for benzene.

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The analytical curve that was plotted from this type of measurement is pictured in Fig. 18. The main cause of the scatter in these points is believed to be the baths used to control the vapor pressure of the benzene. These baths were made by cooling brine solutions of various concentrations with dry ice. It was noted that a variation in temperature occurred during the time of the measurement. In order to determine the reproducibility of the instrument the procedure described above was repeated eight times, using a short path length cell so that the side arm containing benzene could be kept at a constant temperature in an ice bath at zero ^{o}C. The coefficient of variation was 9.5 %.

The data described above demonstrated that this technique is capable of reproducible operation and reliable calibration. It must be remembered that these data were obtained on equipment that was put together mainly to prove the TALMS concept as applied to complex molecules. Better results are expected from instruments that are designed after experience with the present system.

SEARCH FOR TALMS SIGNALS

Having established reliable behavior using benzene and the Hg 253.7 nm line, a search was undertaken to determine other atomic lines that would produce a TALMS signal with benzene and other organics. One phenomenon encountered early in the search was adsorption of sample on the cell walls. This effect became apparent when working with arsenic lines of wavelength less than 200 nm. In this wavelength region absorption coefficients are much larger than at longer wavelengths. It was noticed that after filling the cell with the vapor of an organic compound, several minutes of vacuum pumping were required before the transmission returned to the level that existed before admitting the vapor. The organic vapor was being absorbed by the walls or other parts of the cell and only slowly desorbed while evacuating.

This meant that lack of reproducibility could result because the compound that was in the cell was not necessarily the one that had been purposely introduced. It was found that the slow return to 100% transmission could be rectified by flushing the cell with ozone. The assumption was made that the rapid return to full transmission at short wavelengths (<200 nm) indicated that former organics were purged from the cell. The line-compound list in Table 2 was obtained after first verifying that the cell was clean before each measurement.

TABLE 2. TALMS Lines (Wavelengths in Angstroms)

	HG 2537	CU 2492	AS 2456	CU 2441	AS 2349	CD 2288	AS 2288
Benzene	+	+	+	+	-	-	-
Carbontetrachloride	NT	NT	-	NT	-	NT	-
Chlorobenzene	+	NT	-	NT	-	NT	-
Ozone	-	NT	NT	NT	NT	NT	NT
Pyridine	NT	NT	-	NT	-	NT	-
Toluene	NT	NT	-	NT	-	NT	-

	CD 2144	AS 2113	AS 2003	AS 1972	AS 1937	AS 1890
Benzene	-	(1)	(2)	-	-	-
Carbontetrachloride	NT	NT	-	-	-	-
Chlorobenzene	NT	NT	-	-	-	-
Ozone	NT	NT	NT	NT	NT	NT
Pyridine	NT	NT	-	-	-	-
Toluene	NT	NT	-	-	-	-

+ indicates TALMS signal found
- indicates TALMS signal not found
NT = not tried
(1) = signal very weak
(2) = signal could not be reproduced

The Table contains a larger number of lines giving TALMS signals with benzene than with other compounds. This is because an effort was made to use atomic lines that coincided with sharp benzene absorption features. These results confirm the early estimates that matches are a fairly rare occurrence and, hence, interference is rare. We do note, however, that chlorobenzene was found to interfere with benzene when the Hg 253.7 nm line is used.

LINE SHAPE MEASUREMENTS

An important characteristic of TALMS is the variation of signal intensity with magnetic field strength. It should be recalled that the signal is the difference between two shifted Zeeman components and for this reason it is difficult to relate intensity variations to the structure of molecular absorption. The variation of the intensity of only the sigma + component does represent a scan of the molecular absorption line shape over the wavelength interval corresponding to the shift of this component. Likewise

for the variation of the intensity of the sigma - component. But it is not possible to determine molecular structure if only the difference between these components is known. Nevertheless, the variation of the TALMS signal with magnetic field can be used as qualitative information that will be helpful in identifying species. Whereas the shape of the absorption feature may only be obtained by monitoring the two components separately.

The present instrumentation was designed to display the difference between sigma + and sigma - about 100 times each second. Hence, it is relatively easy to obtain the field dependence of the difference signal. In order to obtain the field variation of the two Zeeman components separately, right and left handed circularly polarized light must be converted to parallel and perpendicular linearly polarized light. The intensity of the two linearly polarized components must then be measured with the sample in and out of the light path. With the sample out of the system we obtain the intensity of the two components when absorption equals zero (I_{o1} and I_{o2}). With the sample in the system we obtain the intensity of the two components (I_1 and I_2) modified by the sample absorption. A plot of I_1/I_{o1} vs H (the field strength) then produces a profile of the molecular absorption over the spectral region scanned by one of the Zeeman components. A plot of I_2/I_{o2} produces a profile over the region scanned by the other component.

A schematic of the system used to make this measurement is displayed in Fig. 19. Polarizer 1 is mounted so that the only light transmitted is polarized at a 45 degree angle to the direction of stress on the phase retardation plate. This angle is chosen so that after proper adjustment of stress, circularly polarized light will be converted to plane polarized light. Polarizer 2 is then mounted so that it can be rotated to either pass or extinguish the light from polarizer 1. The intensity when the polarizers are aligned for maximum transmission is recorded (chart recorder). Next polarizer 2 is rotated so that there is no transmission. Marks are made on the rotating device holding polarizer 2 so that the position of maximum and minimum transmission can be reproduced. With polarizer 2 in the position of minimum transmission, pressure is applied to the phase retardation plate until the intensity reaches 1/2 the value obtained with the polarizers in a parallel position. (until now there had been no pressure on this plate). Polarizer 1 is then removed from the system and the intensities of the two Zeeman components are measured by positioning polarizer 2 to agree with the marks made earlier. The phase retardation plate in this system will now convert circularly polarized light into plane polarized light. First one, then the other Zeeman component will be transmitted as polarizer 2 is rotated to the marked positions.

A check of the quality of the optical set-up may be made by measuring the four intensities. At zero magnetic field the ratios I_1/I_{o1} and I_2/I_{o2} should be equal. If they are not equal, the system should be checked for light that is reaching the photomultiplyer tube without passing though the retardation plate and polarizer. One should not expect I_{o1} to equal I_{o2} because the intensity of reflected plane polarized light from the grating in the monochromator will vary depending on the angle between the groves and

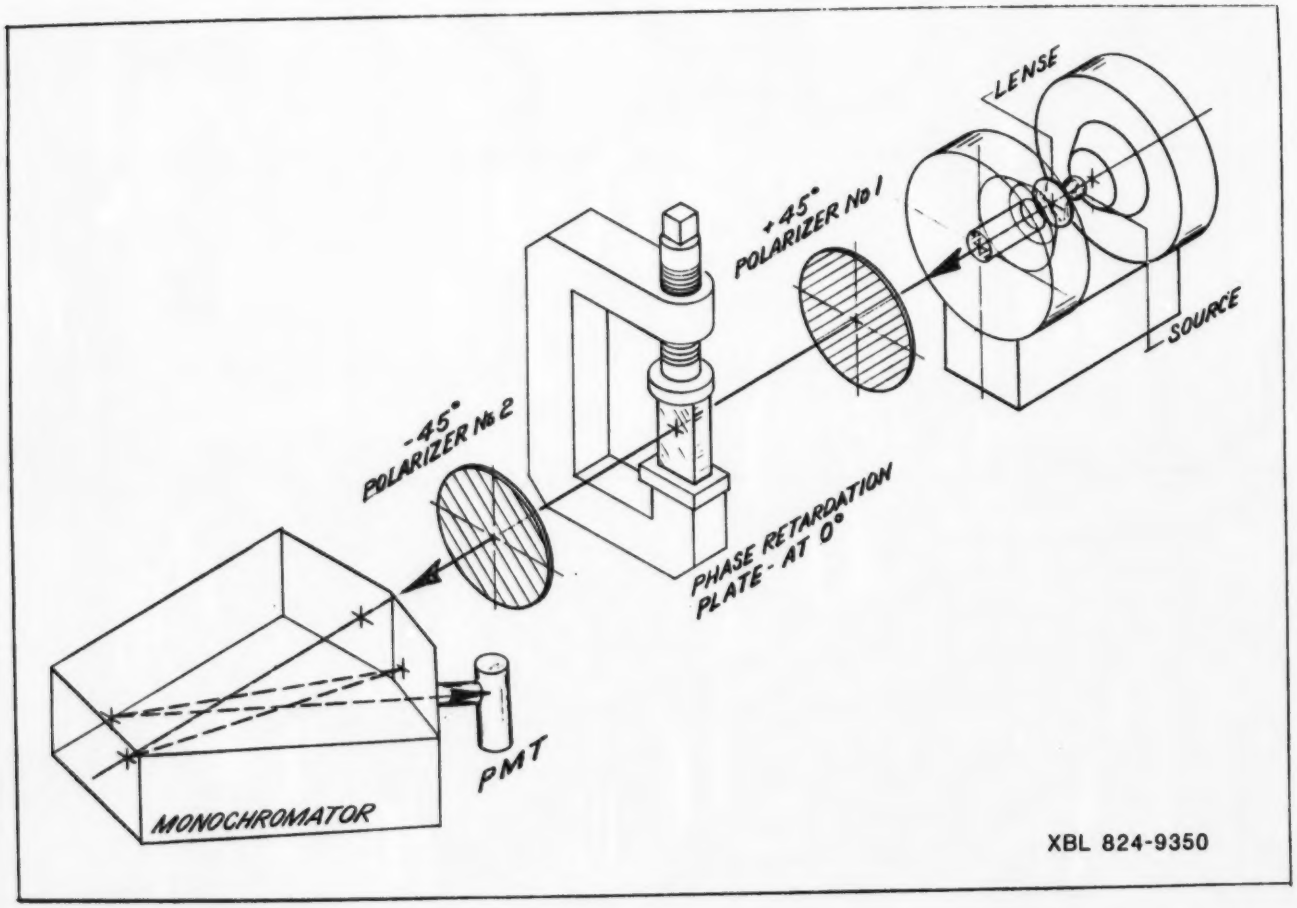

Figure 19. System for the measurement of sigma + and sigma - independently.

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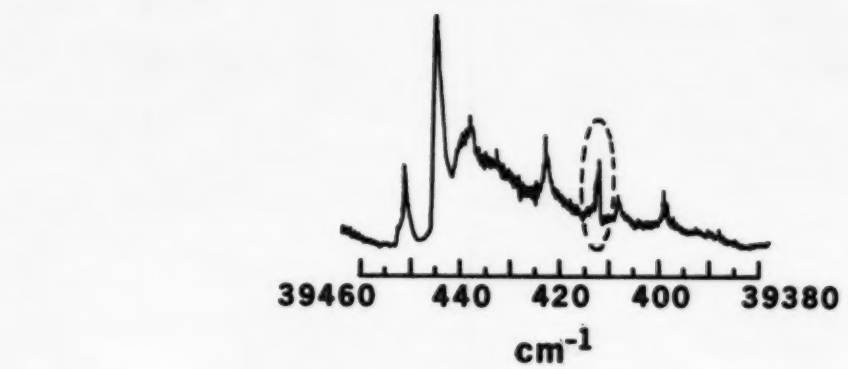

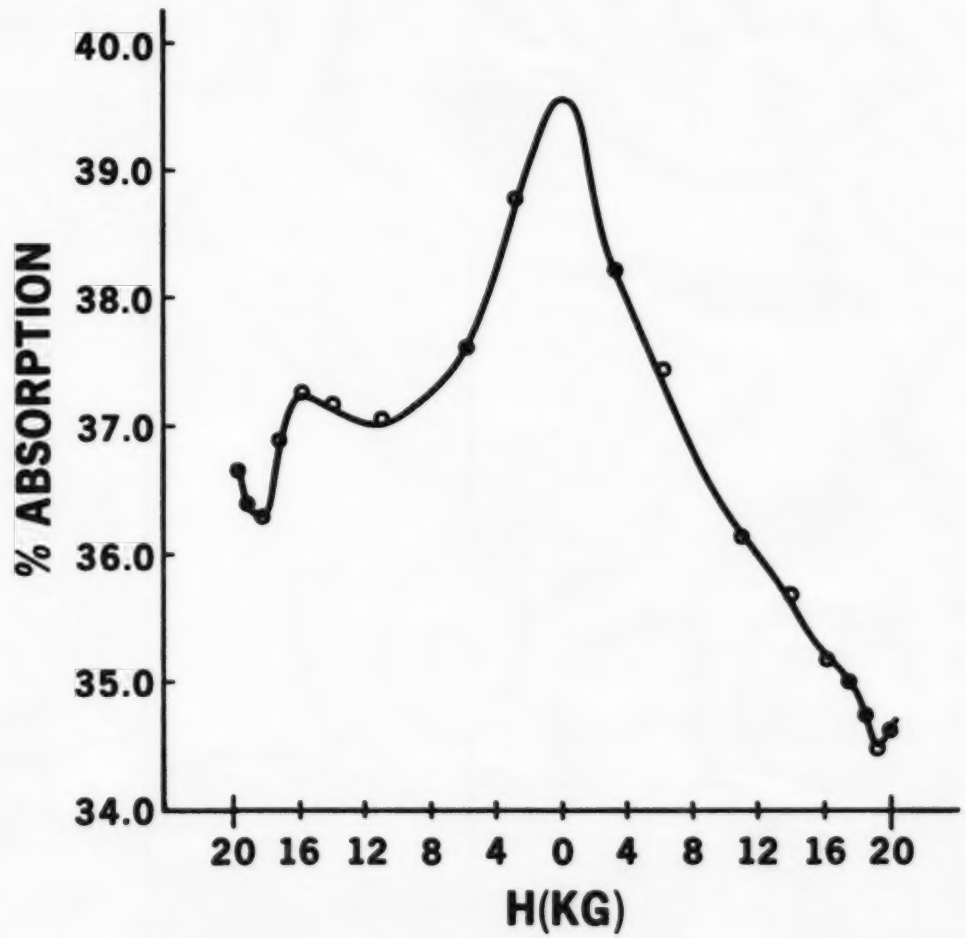

Figure 20. Zeeman scan of benzene compared with high resolution spectrum.

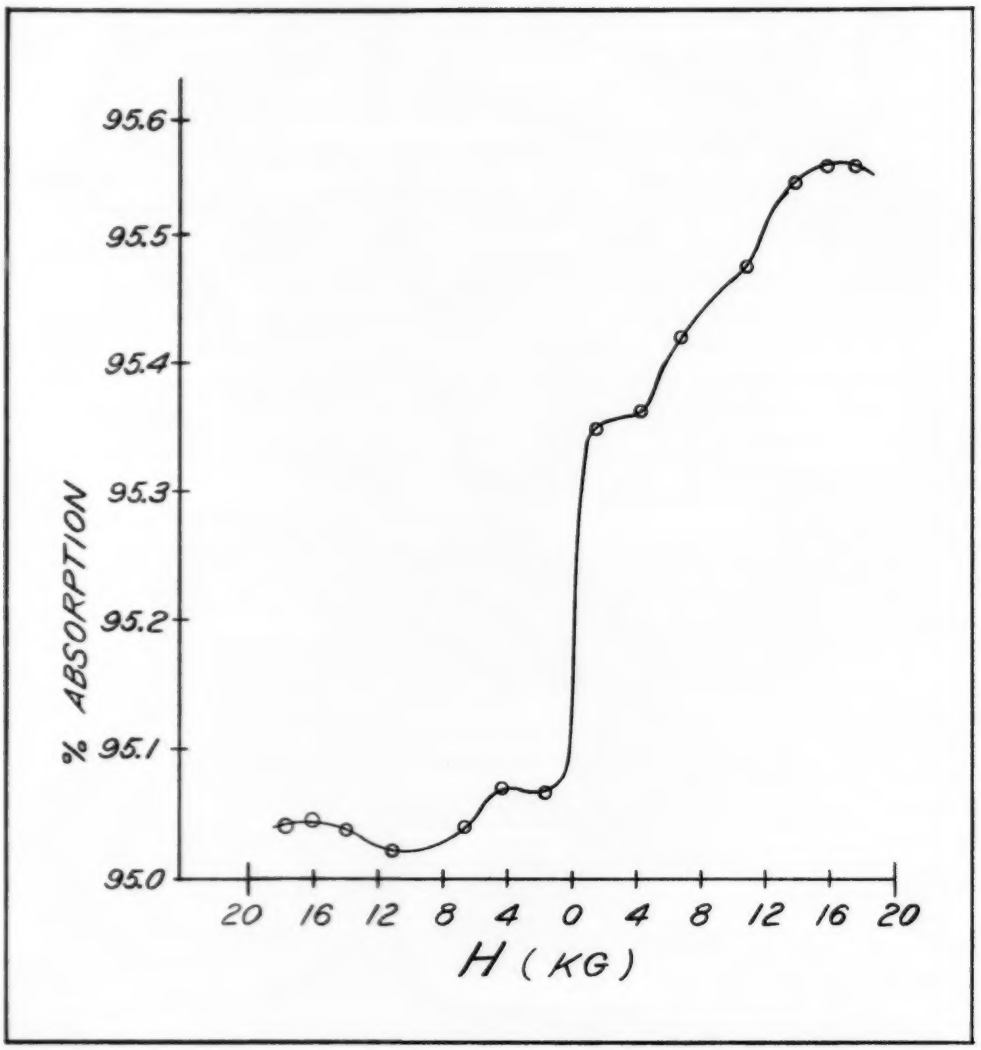

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Figure 21. Zeeman scan of chlorobenzene.

the direction of polarization.

This system was used to determine the line shape of the benzene line at 253.7 nm. The results are displayed in Fig. 20. This scan should be compared with the high resolution spectrum of benzene (upper part of the figure) obtained by Atkinson and Parmenter (Ref. 8). (We are indebted to Don Scott of the EPA at Research Triangle Park for making us aware of this reference). From a knowledge of the g value of the 253.652 nm Hg line and a knowledge of the magnetic field strength over which the scan was made, the wavelength region scanned was found to be 1.5 cm^{-1} on either side of 39,412.30 cm^{-1}. This encompasses the absorption feature circled in Fig. 19. Both spectra reveal a peak with a shoulder. This is another confirmation of the ability of the TALMS technique to obtain high resolution spectra of moderately large molecules. In this case, a factor of two improvement in resolution can be achieved by using a single Hg isotope in the light source. However, this will be of no value if the absorption spectra are already "Doppler limited".

The line shape of chlorobenzene (Fig. 21) was determined in a similar fashion. A number of interesting features are revealed by comparing Figures 20 and 21. First, it is clear that even though both give TALMS signals at the same wavelength, there is little similarity between the magnetic field line shapes. This presents a means of differentiating between these two molecules with out changing light sources. (The fact that benzene yields a TALMS signal with the As 245.6 nm line and chlorobenzene does not is another way of differentiating). Second, chlorobenzene could be monitored in the presence of benzene by using low magnetic fields around a Hg light source. This is true because the benzene line shape is symmetrical about zero field until fairly high field strengths are reached; whereas chlorobenzene is not at all symmetrical at low fields. Third, the line shape of the benzene molecule peaks very close to zero magnetic field. This indicates that a more sensitive benzene detector could be constructed by utilizing the perpendicular Zeeman effect rather than the parallel Zeeman effect. (In this case the unshifted pi component and shifted sigma components would be used to make the measurement).

This type of information emphasizes the value of line shape determinations. They will be very useful in the design of a more compact instrument for delivery to the EPA.

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APPENDIX I
MECHANICAL DIAGRAMS

A block diagram of the TALMS instrument is given in Figure 22. The complete experimental layout is shown in Figure 13 and a photograph of the assembled instrument is shown in Figure 23. The mechanical and electrical connections are shown in a diagram in Figure 14.

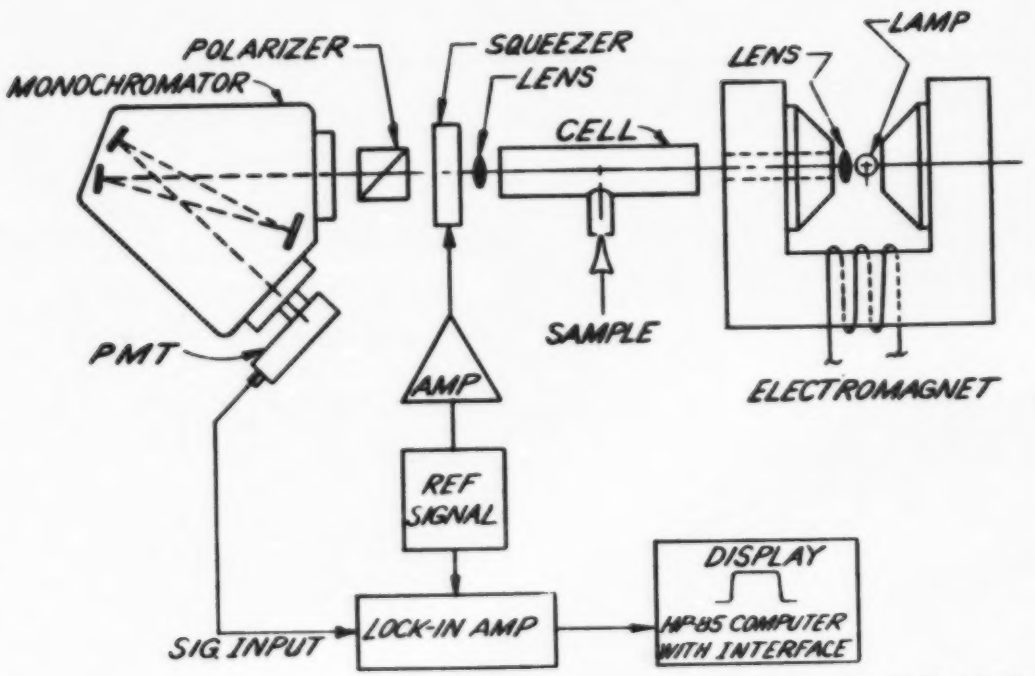

Figure 22. Block diagram of TALMS instrumentation.

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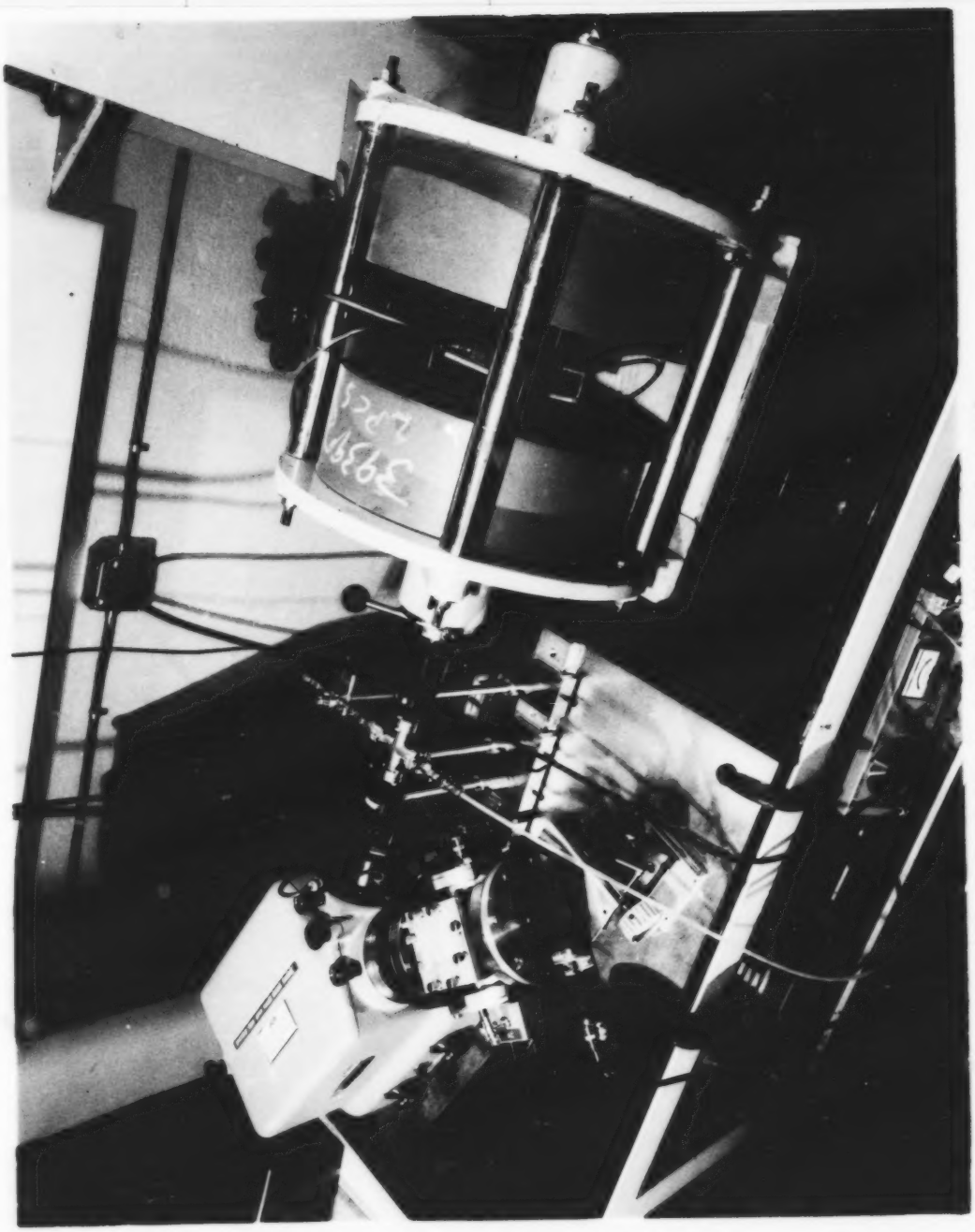

Figure 23. Photograph of the assembled TALIS instrument.

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APPENDIX II
ELECTRONICS DIAGRAMS

A block diagram of the signal processing electronics is shown in Figure 24. A diagram of the manual controls on the electronic module bin is given in Figure 25. Electronic diagrams for the lamp driver and the lock-in amplifier are shown in Figures 26, 27 and 28. The magnetically confined lamp and the low frequency discharge lamp are shown in Figures 9 and 10. A photograph of the phase squeezer is shown in Figure 12.

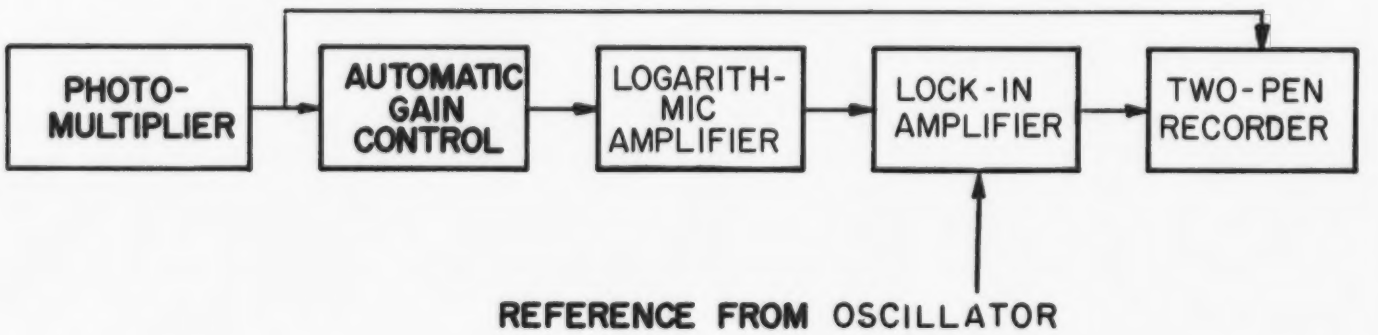
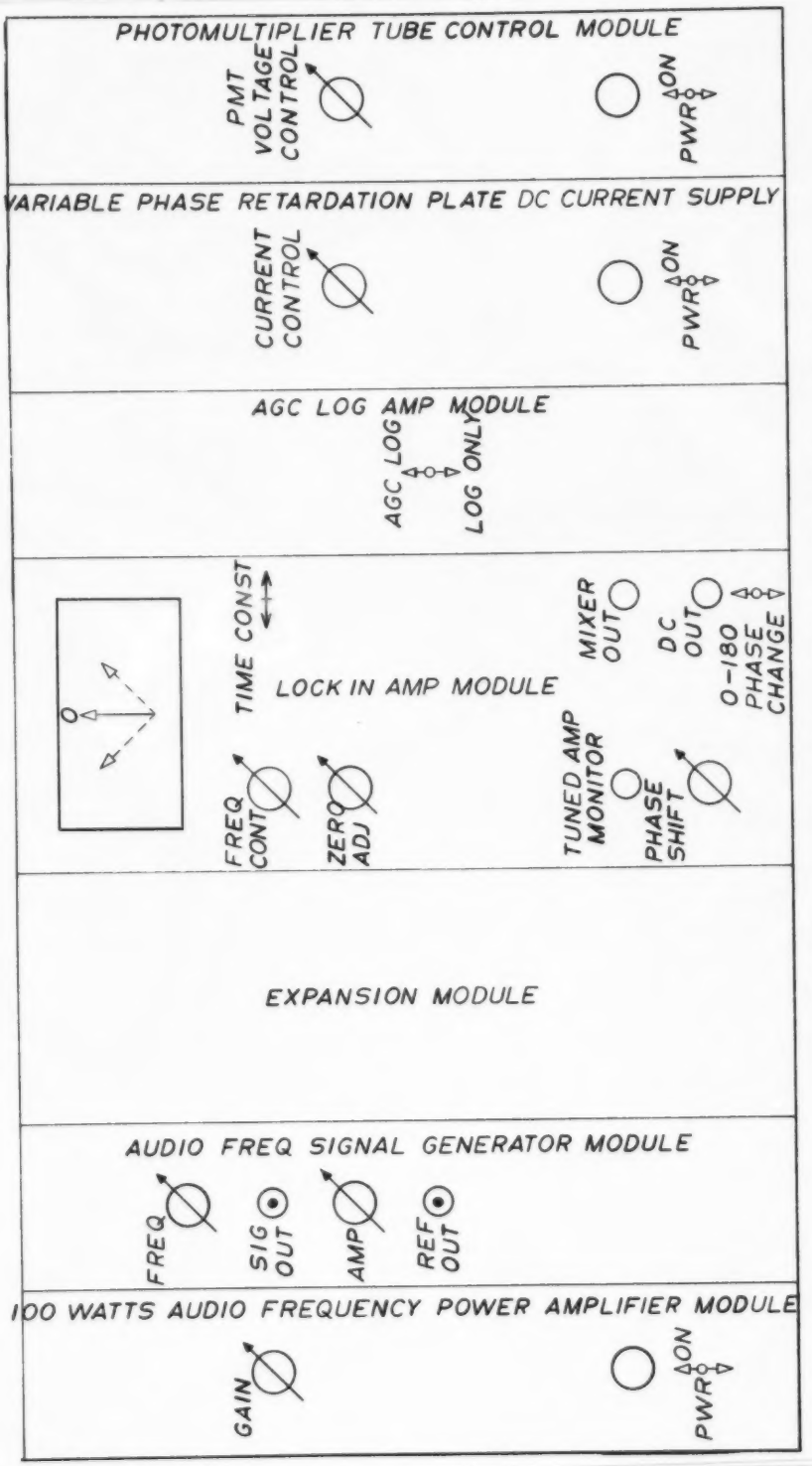


Figure 24. Signal processing electronics.



ELECTRONIC MODULE BIN - FRONT VIEW

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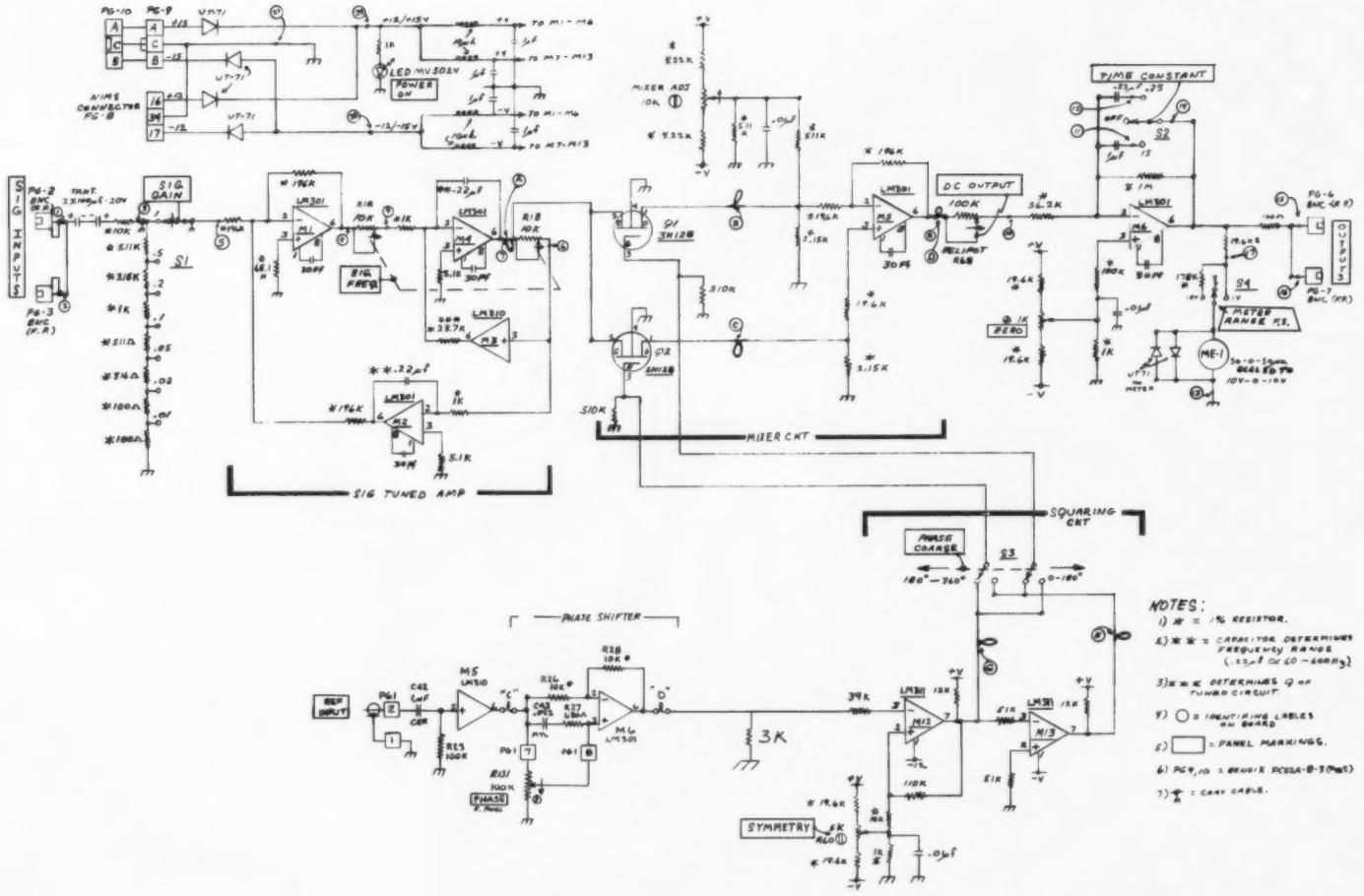
Figure 25. Front view of the electronic module bin showing the manual controls.



LOCK IN AMP

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Figure 26. Circuit diagram of the TALMS lock-in amplifier designed and constructed at LBL.

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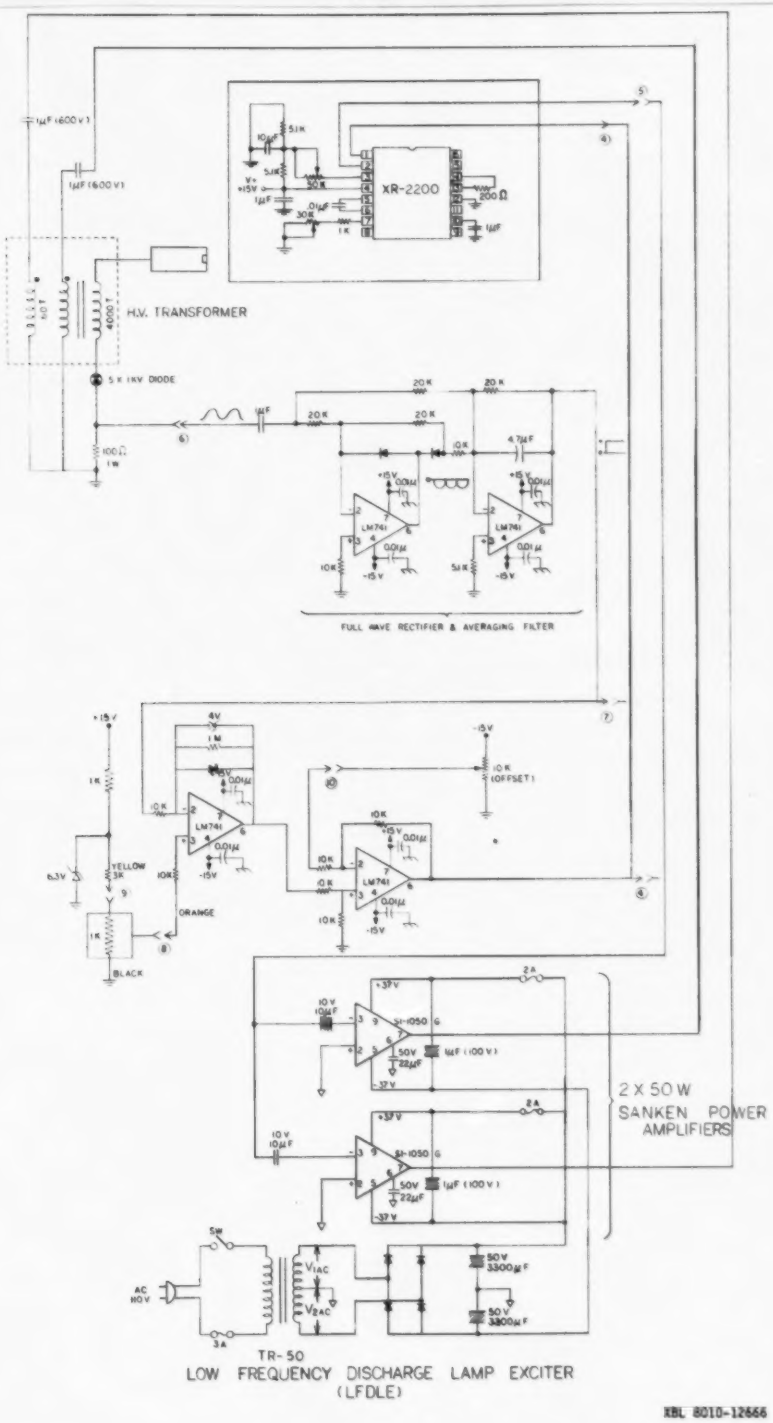

Figure 27. Circuit diagram for lamp driver.

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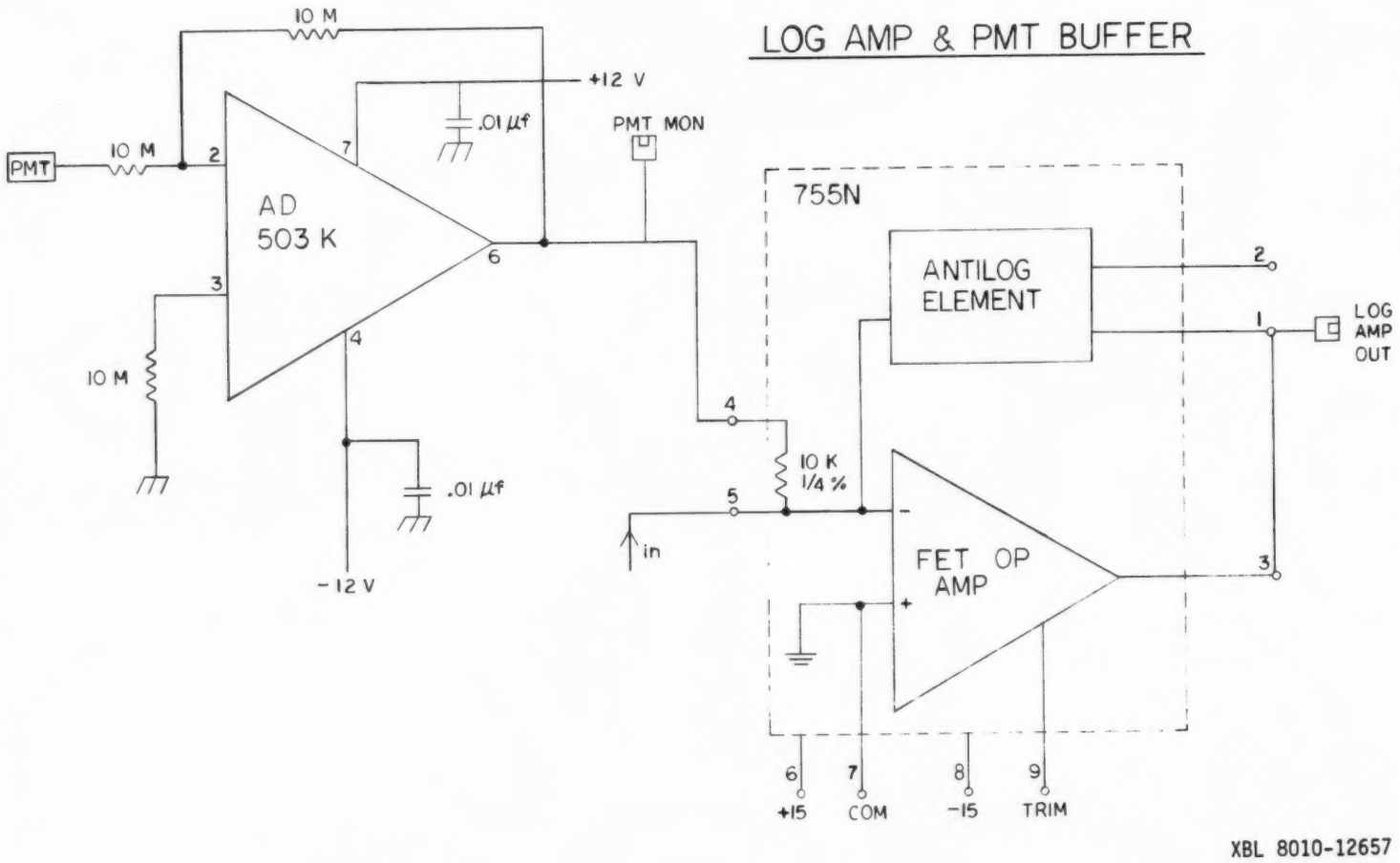

Figure 28. Wiring diagram for the logarithmic amplifier. The TALMS instrument may operate with or without the automatic gain control feature shown in Fig. 26.